

METHANOL SYNTHESIS IN A THREE PHASE REACTOR. Dr. Martin B. Sherwin, Dr. David B. Blum. Chem Systems Inc., 275 Hudson Street, Hackensack, New Jersey 07601.

Chem Systems, under the sponsorship of the Electric Power Research Institute, is developing what it considers to be both an efficient and reliable system to manufacture methanol for peak shaving power generation from coal-derived synthesis gas. The reaction scheme consists of a three-phase fluidized bed reactor. Synthesis gas containing CO, CO₂ and H₂ is passed upward in the reactor cocurrent to an inert liquid which serves to both fluidize the catalyst and absorb the exothermic heat of reaction. The conversion level is limited by equilibrium considerations but a close approach should be obtainable by this system. At 800-1000 psig and 260°-300°C, about 25-30% conversion should be realized by utilizing a commercially available copper-based catalyst. The exothermic heat of reaction is taken up by the liquid as sensible heat and by vaporization. The overhead product gases are condensed to remove the product methanol and water and to recover any vaporized liquid for recycle. The main liquid flow is circulatory through a heat exchanger for temperature control. Unreacted synthesis gas can either be recycled to the reactor or burned directly for base-load power generation.

COPRODUCTION OF METHANOL AND SNG FROM COAL:
A ROUTE TO CLEAN PRODUCTS FROM COAL
USING "READY NOW" TECHNOLOGY

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INTRODUCTION

Clean fuels and chemicals have been produced from coal for more than a century. When natural gas and crude oil became readily available at low cost, coal use decreased. In most of the developed countries, only limited research and development efforts continued. However, where gas and oil were not readily available and coal was, the development has continued, and today we have three primary processes to convert coal into a synthesis gas which can be cleaned up to remove sulphur and other objectional impurities and which can be used as a fuel as is, upgraded to a pipeline quality or high Btu gas or converted into other products (liquid fuels or chemicals). The main processes in use today on a commercial scale are the Winkler, the Koppers Totzek, and the LURGI process. These processes are competitive, and the choice for any particular application is made on both the quality and characteristics of the coal available and on the products desired.

Many other processes are in various stages of development--bench scale, pilot plant, and demonstration plant--but none are in full scale commercial operation, nor have any of them been selected for full commercial scale plants that have been announced. I am excluding all of these from "ready now" technology on the basis that no companies or investors have selected any of the new processes for major new plant investments. Of those plants announced for construction in the United States, the majority have selected the LURGI process. These plants are designed to produce high Btu gas essentially equivalent to natural gas for augmenting the diminishing supplies of natural gas being produced in the United States.

The Winkler and Koppers Totzek processes produce a gas from coal consisting essentially of carbon monoxide and hydrogen as worthwhile and usable constituents. These

processes minimize the production of by-products such as tars, phenols, naptha, etc.

The LURGI process, which operates at substantially higher pressures, produces in addition to the carbon monoxide and hydrogen, a substantial amount of methane and also substantial quantities of ammonia, naptha, phenol, and tars. The amount of methane, depending on the type of coal being used, can be as high as 33% of the methane, CO and hydrogen produced.

The writer and his associates were working on and trying to develop an economic production facility for SNG from a specific Western coal. We had decided that the LURGI technology was the best for our particular conditions, coal feed and desired product. The particular coal that we were using resulted in a 1-1-2 mol ratio of methane, CO and hydrogen. We were intrigued by the CO-hydrogen ratio which is stoichiometrically what is required to produce methanol, and we therefore decided to evaluate a project which would make methanol out of the carbon monoxide and hydrogen and save the methane for our original purpose, and that is, the production of SNG for addition to the U. S. natural gas supply.

The equipment, processing steps, etc. for cleaning up the synthesis gas produced from coal proved to be essentially the same, whether we converted the gas to SNG via a methanation step or whether we converted it to methanol using existing technology. We therefore developed capital and operating cost figures for a coproduct plant producing SNG and methanol for comparison with our already completed SNG from coal plant. We elected not to make a third study, and that is the production of methanol, only, from the synthesis gas produced from the coal, but studies on this subject have been made by others, and one of the papers in this session covers such a study. The reason we did not conduct the third study was because we felt that the much lower thermal efficiency going from coal to methanol would not be anywhere

near as economically attractive as the coproduct plant or the straight SNG plant. The lower Btu efficiency of a methanol from coal plant, between 45 and 50%, are confirmed by Dr. Dennis Eastland of Davy Powergas in his paper at this session.

We believe that our evaluation shows that there are some substantial advantages for the coproduction of SNG and methanol and that a very large advantage exists if the methanol can be sold at a premium price above fuel value as it historically has sold and currently sells as a chemical, rather than a fuel.

This report will describe the similarities and differences between a plant to produce SNG and a plant to produce methanol and SNG.

* * * * *

TECHNOLOGY

Exhibits 1 through 7 summarize technology, capital and operating cost of a coal derived coproduct SNG/methyl fuel project compared to a coal derived SNG project alone.

It should be pointed out at the outset that these studies do not include capital or operating costs of developing a mine.

Exhibit No. 1, an abbreviated block flow diagram, depicts a simplified flow configuration on a LURGI technology based coal gasification project. This is a typical configuration and is almost identical with that in the Wesco coal gasification filing and with much fundamental similarity in the El Paso gasification schemes as submitted to the Federal Power Commission (although there are some differences). The point to be made here is that all process steps are commercially proven.

Output in this case is a standard 250 M²SCFD of SNG at 987 HHV with an input of 30,079 ST/D of Buffalo, Wyoming, coal, which is the basis of a study conducted for Transco by Fluor. There are some 8,100 BPD of liquid fuel by-products as fuel oil, naptha and tars. 150 ST/D sulphur is produced,

180 T/D ammonia and 114 T/D phenols.

Exhibit No. 2 shows a block flow diagram of how this existing study configuration would be modified for coproduction of SNG and methanol. It is to be remembered that the whole coal gasification process would still be based essentially on LURGI coal gasification technology.

In this exhibit, the red cross hatching indicates identical battery limits units (inside the gasification complex) compared to SNG only. The green indicates units and systems that would change in size--more or less. The blue cross hatching would be units that are net additions needed to realize the fuel coproducts.

The methanol synthesis technology for this report has been evaluated from information received from Imperial Chemical Industries, Ltd. (ICI), who are licensors of a methanol process. ICI has reviewed the Transco concept for the methanol yield data.

Gross coal input for the coproduct mode is 33,185 ST/D, some 10% more than the straight SNG mode. The quantity of gasification feedstock would remain the same for either mode, but the increased quantity of coal in the coproduct mode is required for the increased steam and power requirements.

All other by-products such as the liquid fuels, sulphur, ammonia and phenols, would be produced in exactly the same quantity as in the SNG alone mode.

Exhibit No. 3 makes a three-way thermal efficiency comparison between the two modes. The first compare Btu's produced per day in prime fuels only. In this case, the co-product mode produces 4.33% more than SNG alone. (Of the total co-product, 59% is SNG and 41% is methanol).

In the second comparison, the thermal efficiency of total fuel and process coal feed (no by-products) is considered. Here, the SNG single product has an advantage of about 2.8%.

In the third comparison, the total products (except sulfur and ammonia) are considered. This results in a greater differential (3.79%) in favor of SNG alone.

CAPITAL AND OPERATING COSTS

Exhibit No. 4 shows conceptual capital cost comparisons between the two modes in the general category of process units, utility and offsite units. Basis of the cost data is the Fluor report, in turn, derived from the Wesco work. Costs are taken as 1974 basis. It can be seen that the dollar changes between the modes are minimal with the greatest effect in the addition of the methanol synthesis loop and purification. Net dollar addition is \$25,118 M for the co-product mode.

In the utility units, a large change is the elimination of the compression step in SNG but the addition of more steam generating and water related facilities. Net dollar addition is \$15,026 M.

The offsite costs are virtually the same with the exception of tankage and this has been increased in the co-product mode to provide two weeks' inventory of methanol fuel. Dollar differential is \$3,002 M.

Exhibit No. 5 summarizes capital cost of both modes in the three general categories, and shows the effects of such additives as sales tax, initial charge of catalysts and chemicals, fees and royalties, railroad

spur, environmental, spare parts, water supply, working capital, interest during construction and contingency. Net dollar differential after final addition is \$59,679 M.

Exhibit No. 6 on the operating cost estimate shows the comparative cost for the first full year of operation, 1974 basis. This example shows the effect of total coal feed at $30\text{¢}/\text{M}^2\text{Btu}$ with the addition of catalyst and chemicals, wages, overheads, maintenance supplies, ash disposal, taxes and insurance and water supply. Credits are given in this line-up for the values of the by-products which, as can be seen, are the same either case.

As a matter of interest, the operating cost reflects an organizational roster of 620 people for SNG alone versus 650 people in co-product.

It should be remembered that these studies exclude mine operating and development costs and that these are covered by the purchase price of the coal. The subsequent economic studies reflect the capital costs, operating cost and the effects of varying the coal costs.

The question has been raised as to the effects of reducing the co-product facility size to reduce capital dollar requirement. For this purpose, a facility to produce an arbitrary 2,000 ST/D product methanol with corresponding $56.67 \frac{2}{\text{Mscfd}}$ of SNG output has been cost evaluated. The seventh exhibit shows a resulting capital cost-size plot. In general, reducing the production size from the prime study point by 63% cuts capital cost about 50%. The corresponding coal requirement reduces from 33,200 ST/D to 12,200 ST/D. Subsequent discussions on economics will show the effects of size reduction on product value.

ECONOMICS

The economic analysis which is presented looks at the co-production

of methanol and SNG on two bases, one which assigns the same value to a Btu regardless of the product form and the other which recognizes the real world historical pricing relationship between the cost of clean liquid fuels and natural gas. Clean liquid fuels have historically sold at a substantial premium over natural gas. Currently, this premium is about \$1 per million Btu. Chemical methanol, which can be produced for a negligible additional cost, has sold at a substantial premium above clean liquid fuels on a contained Btu basis.

The economics show that if a clean liquid fuel or a chemical methanol market price can be obtained, the co-product plant can produce a greater return on capital investment and requires less capital investment per dollar of annual sales, or a lower sales price for the SNG.

Exhibit No. 8 shows that on a combined total Btu basis, SNG alone appears the more attractive venture. SNG/methanol co-production requires a product price of about 8% more per million Btu and costs \$60 MM more to build.

Exhibit No. 9 shows what the minimum required SNG price would be at different methanol prices to give a 20% return on equity. As an illustration, select a point which is near today's open market prices: coal at 90¢/MMBtu and gas at \$1.48/MMBtu. Minimum required methanol price would be \$6.00/MMBtu or 38.9¢/gal. Current price of methanol is 32¢/gal.

Exhibit No. 10 shows the same information in graphic form.

For the reduced size plant discussed in the technology section, we have also calculated the average required sales price for the products based on Btu content as shown below:

	Required Sales Price - \$/MMBtu	
	Methanol Rate, ST/D	
Coal Price - c/MMBtu	5420	2000
30	2.12	2.44
60	2.73	3.05
90	3.34	3.66
SNG Rate - MMSCF/D	154	57

ECONOMICS - BASES AND ASSUMPTIONS

1. 20% DCF internal rate of return on equity.
2. Financing provided on a 70/30 debt/equity ratio.
3. Interest rate of 9% per year on all debt, both construction and long-term.
4. Book depreciation done on straight line basis.
5. Tax depreciation done on double declining balance with normalization basis.
6. Sinking fund payments 5% per year on a semi-annual basis.
7. Five-year construction period and 25-year operation period.
8. Startup 1 January 1974.
9. Operating and maintenance costs constant for 25-year plant life.
10. Coal feed assumed to be available at plant inlet at a given purchase cost.
11. For combined total in Exhibit No. 8, Btu prices were apportioned into the expected split of 59% SNG and 41% methanol.

METHANOL MARKET - FUEL

Gasoline substitute is the greatest potential market for fuel grade methanol. It is so great that the largest conceivable plant would supply less than 3% of the market. However, the introductory problems to this market are almost insurmountable for the near future, except for possibly a captive fleet (i.e., New York City taxis).

The market that would be served first appears to be peaking turbine fuel. This is the conclusion of government agencies, supported by G. E. and Westinghouse confirmation that methanol has 7% higher efficiency and 6% more KW than fuels being used at present.

Exhibit No. 12 shows some statistics looking at specific areas and markets. Electric utility boilers not requiring conversion (gas burning) in Texas and Louisiana alone would consume 5,900 tons/day of methanol. Boilers requiring conversion (oil burning) in the same area would require 177,000 tons/day. And gas turbines would require 2,260 tons/day.

Our two large customers would consume a combined total of about 5,500 tons/day in their gas turbines. In yet another use, Transco compressors to transport one trillion CF/year would require 6,300 tons/day.

Exhibit No. 13 shows the total U. S. peaking fuel requirement for electric utility gas turbines and internal combustion engines. The daily requirement of methanol would be 32,000 tons for gas-burning turbines and 62,800 tons for oil-burning turbines.

The 1974 electric utility consumption of all fuels for gas turbines used to generate electricity is equivalent to more than 100,000 tons per day of methanol. Methanol has a 7% thermal efficiency advantage over the fuels that are currently being used (natural gas, LPG's, #1 and #2 fuel oil and JP). The increased thermal efficiency results from the higher

mass flow through the turbine (approximately 2%) and from the use of vaporized methanol (approximately 5%). Liquid methanol boils at 64.65° C. and can be vaporized with waste heat from exhaust gas that is at too low a temperature for any other economic use. Methanol's advantages over these conventional fuels for this use should price it at a modest premium versus these fuels.

Another type of guarantee that will be necessary for a coal/methanol/SNG project will be some form of downside market price guarantee which we presume can only be furnished by the U. S. government. The joint methanol fuel report prepared by a group of governmental agencies and bureaucracies has recognized that such guarantees will be necessary for such a project to become a reality. This government report also recognizes the need for a substantial decrease in the time required for obtaining all of the government-required approvals.

METHANOL MARKET - CHEMICAL

The current United States production of methanol is approximately 12,500 short tons per day. The existing chemical use market is growing at approximately 10% per year. The current supply-demand imbalance amounts to a shortage in excess of 1,000 tons per day. No new plants are under construction. Only one plant is being designed (Celanese's Bishop, Texas plant; estimated additional production capacity: 1,500 tons per day). Exhibit No. 14 shows a profile of the chemical methanol market.

Essentially, all chemical methanol produced in the U. S. today is made from natural gas. The natural gas consumption by these plants is approximately 500 MMCF per day.

The posted selling price for methanol at the end of the third quarter of '74 was 32¢ per gallon (\$5/MMBtu) FOB producing plant, but none was available at this price. The drastic downturn in the home building and

automotive market (which account for over one-half of all methanol consumption) has created a surplus of supply over demand. Short of a long term recession, additional chemical production will be needed at near its historical growth rate.

The future cost of chemical methanol calculated on a Btu value cannot be less than the cost of 1.8 Btu of purchased natural gas plus \$1.00 per million Btu of methanol produced. For example, if natural gas is \$2.00 per million Btu, the cost of methanol would be \$3.60 for natural gas plus \$1.00 for plant cost for a total of \$4.60 per million Btu. Most U. S. methanol is produced from intrastate gas for which sales have been reported as high as \$2.05 per MMBtu in 1975.

For these reasons, we believe that methanol sold in the chemical marketplace will continue to command its historic premium price over the cost of clean liquid fuels. We believe that this premium will amount to a minimum of \$1.00 per MMBtu. On this basis, chemical methanol price can be expected to at least maintain its current price. We believe that the current price of clean liquid fuels is between \$2.00 and \$2.50 per million Btu.

Therefore, to the extent that methanol can be sold in the chemical market, this will represent the highest price which can be obtained.

Because of the domestic shortage of natural gas, even in the intrastate market, the chemical producers with whom we have had conversations believe that chemical methanol will be produced from coal in the United States in the 1980's.

CONCLUSIONS

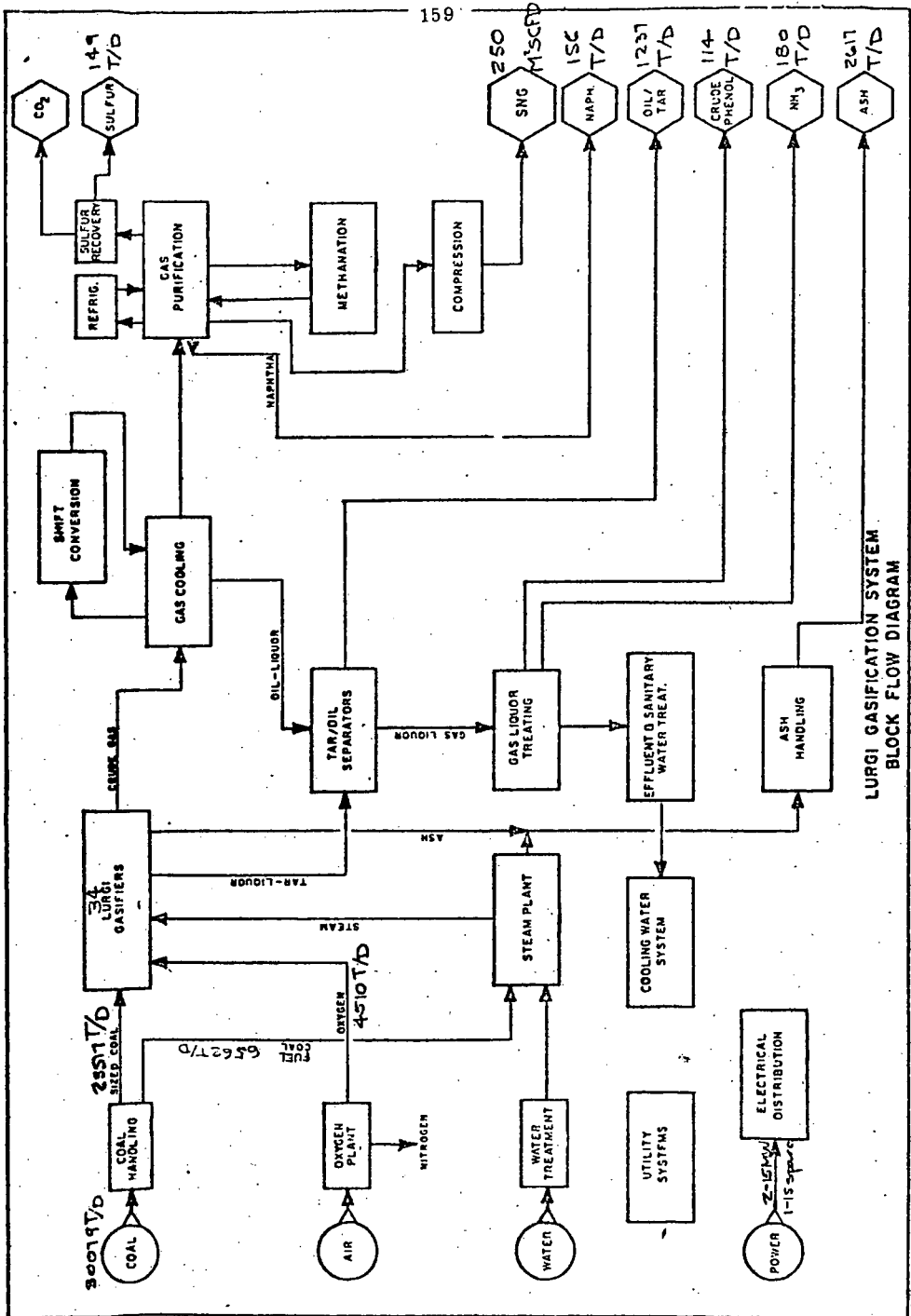
On the concept grade evaluation that has been made, we conclude that further in-depth effort should be made:

1. To produce feasibility grade capital and operating cost and product cost,
2. To evaluate marketing potential for the products (SNG and methanol), and
3. To obtain governmental encouragement and support for such a venture by the private venture or free enterprises energy production interests.

ACKNOWLEDGEMENTS

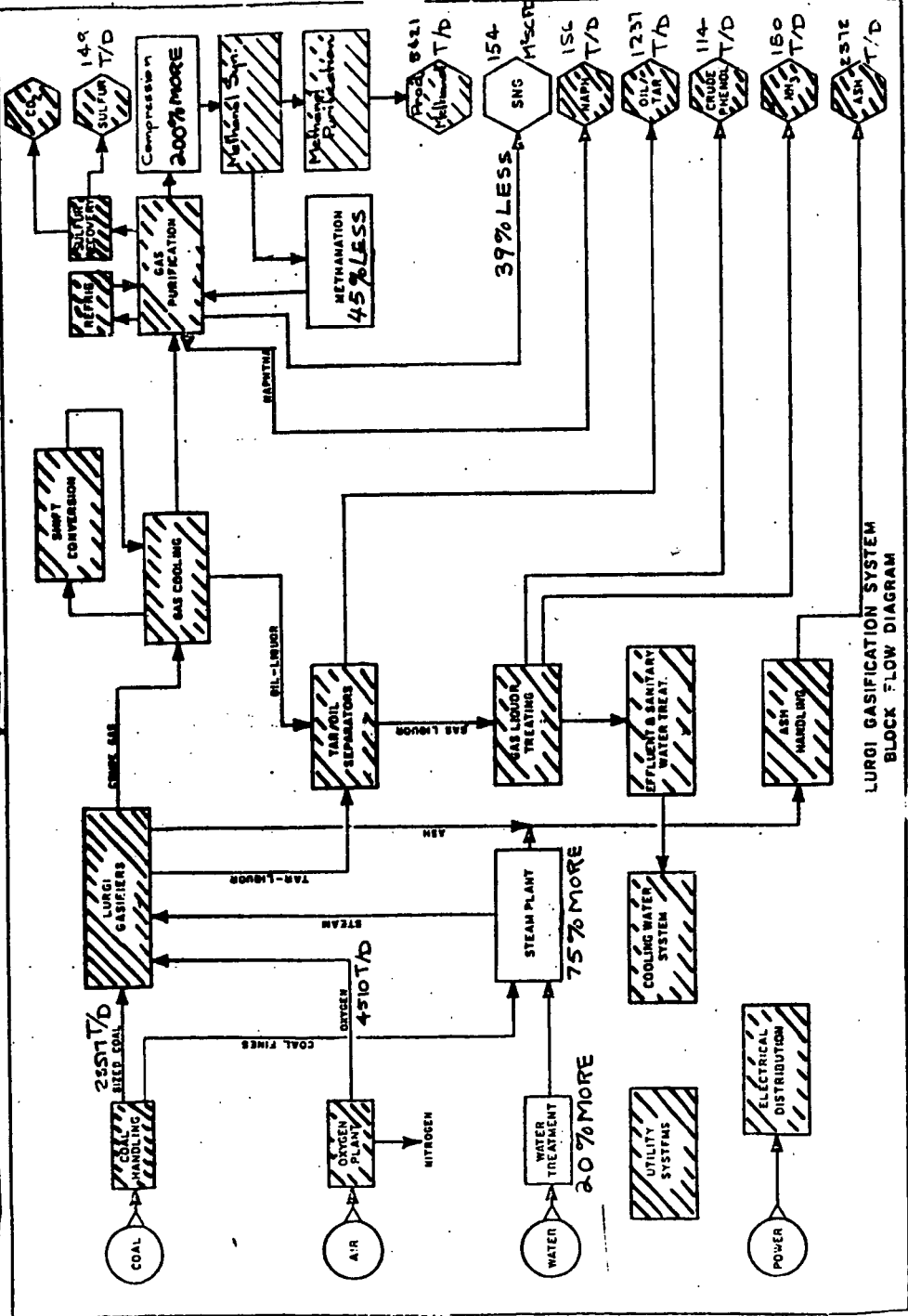
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Lawrence Livermore Laboratory



LURGI GASIFICATION SYSTEM
BLOCK FLOW DIAGRAM

SNG Alone



C₆-Fuel-Methanol/SNG

EFFICIENCY COMPARISONS
SNG VS SNG/MeOH FROM COAL

I. PRIME END PRODUCTS ONLY

SNG/MeOH:

$$\begin{array}{rcl} \text{SNG} & - & 153.611 \text{ M}^2\text{scfD @ } 987 \text{ Btu/scf} = 151.614 \text{ M}^3\text{BtuD} \\ \text{MeOH} & - & 5420.8 \text{ T/D @ } 9760 \text{ Btu/lb} = 105.814 \text{ M}^3\text{BtuD} \\ & & \underline{257.428 \text{ M}^3\text{BtuD}} \end{array}$$

SNG ALONE:

$$\text{SNG} - 250 \text{ M}^2\text{scfD @ } 987 \text{ Btu/scf} = 246.750 \text{ M}^3\text{BtuD}$$

COMPARISON:

$$\begin{array}{l} \text{Difference} = 257.428 - 246.750 = 10.678 \text{ M}^3\text{BtuD Benefit from Co-Product} \\ \text{Or} = 4.327\% \text{ increase over SNG alone.} \end{array}$$

II. PRIME END PRODUCTS VS FUEL INPUT

SNG/MeOH:

$$\begin{array}{rcl} \text{Feed coal of } 23517 \text{ T/D @ } 7618 \text{ Btu/lb} & = & 358.305 \text{ M}^3\text{Btu} \\ \text{Fuel; boiler, power, SH. - } 9668 \text{ T/D @ } 7320 \text{ Btu/lb} & = & 141.540 \text{ M}^3\text{Btu} \\ & & \underline{499.845 \text{ M}^3\text{Btu}} \end{array}$$

$$\text{Produces} - 257.428 \text{ M}^3\text{BtuD; Efficiency} = 51.50\%$$

SNG ALONE:

$$\begin{array}{rcl} \text{Feed coal of } 23517 \text{ T/D @ } 7618 \text{ Btu/lb} & = & 358.305 \text{ M}^3\text{BtuD} \\ \text{Fuel; boiler, power, SH. - } 6562 \text{ T/D @ } 7320 & = & 96.068 \text{ M}^3\text{BtuD} \\ & & \underline{454.373 \text{ M}^3\text{BtuD}} \end{array}$$

$$\text{Produces} - 246.750 \text{ M}^3\text{BtuD; Efficiency} = 54.31\%$$

III. ALL END PRODUCTS VS FUEL INPUT

SNG/MeOH:

$$\begin{array}{rcl} \text{Feed \& Fuel} & = & 499.845 \text{ M}^3\text{BtuD} \\ \text{Products: } 257.428 + 49.428 & = & 306.856 \text{ M}^3\text{BtuD} \\ \text{Efficiency} & = & 61.39\% \end{array}$$

SNG ONLY:

$$\begin{array}{rcl} \text{Feed \& Fuel} & = & 454.373 \text{ M}^3\text{BtuD} \\ \text{Products: } 246.750 + 49.428 & = & 296.178 \text{ M}^3\text{BtuD} \\ \text{Efficiency} & = & 65.184\% \end{array}$$

CONCEPTUAL CAPITAL COST SUMMARY

(1974 Costs)

	SNG ONLY 250 M ² scf/D	SNG/MeOH 153.61 M ² scf/D/5421 st/D
Process Units	\$ 186,631 M	\$ 211,749 M
Utility Units	115,815	130,841
Offsites	57,829	60,831
SUBTOTAL	\$ 360,275 M	\$ 403,421 M
Sales Tax @ 1.155%	\$ 4,161 M	\$ 4,660 M
Initial Charge - Catalyst & Chemical	2,650	5,210
Fees, Royalties & Eng.	5,200	5,200
Fees, Royalties & Eng.	---	1,500
Railroad Spur	4,700	4,700
Environmental	1,000	1,000
Spare Parts	1,801	2,017
Water Supply	12,000	13,500
SUBTOTAL	\$ 391,787 M	\$ 441,208 M
Working Capital	10,772	14,920
Interest During Construction	61,979	63,147
Contingency	39,179	44,121
TOTAL	\$ 503,717 M	\$ 563,396 M

- DOES NOT INCLUDE:
1. Construction camp
 2. Product SNG pipe lines (nor \$ difference for size differences)
 3. Loadout and handling for MeOH
 4. Escalation
 5. Startup Costs
 6. Land
 7. Mine & support facilities

CONCEPTUAL COST EVALUATION
(1974 Costs)

SNG FROM COAL VS SNG/METHANOL FROM COAL
(BASIS: FLUOR FEASIBILITY STUDY)

<u>PROCESS UNITS</u>	<u>SNG ONLY</u>	<u>SNG/MeOH</u>
Gas Production (Lurgi)	\$ 65,533 M	\$ 65,533 M
Shift Conversion	10,061	9,000
Gas Cooling	8,739	8,739
Rectisol (Gas Purification)	66,783	65,783
Methanation	22,021	12,100
Phenosolvan (Ammonia - Phenol separation)	13,494	13,494
Methanol Loop	---	37,100
Ethylene Conversion	---	---
TOTAL	\$186,631 M	\$211,749 M
<u>UTILITY UNITS</u>		
N ₂ Compression	\$ 5,370	\$ ---
Oxygen Plant	36,282	36,282
Sulfur Recovery	4,693	4,693
Steam Gen. & Dist.	43,009	61,000
Plant & Instrument Air	525	525
Demineralized Water	3,188	4,391
Fuel Gas & H ₂	380	380
BFW & condensate	3,189	4,391
Ammonia Disposal	789	789
Fly Ash Collection & Fuel Gas Trm.	16,485	16,485
Stacks & Chimney	855	855
Dust Control	1,050	1,050
TOTAL	\$115,815 M	\$130,841 M
<u>OFFSITES</u>		
Site Development	\$ 8,176 M	\$ 8,176 M
Coal & Fly Ash Conveying	5,744	5,744
Electrical System	16,506	16,560
Flares	2,483	2,483
Buildings	4,438	4,438
Fire Water	2,147	2,147
Mud Water	25	25
Fuel Oil	481	481
Cooling Water	2,665	2,665
Clarified Water	834	1,150
Plant & Potable Water	1,101	1,101
Loading & Unloading	529	529
Holding Pond	1,420	1,420
Proc. Effluent Treat	8,750	8,750
Tankage	1,796	4,428
Sulfur Storage	734	734
TOTAL	\$ 57,829 M	\$ 60,831 M

OPERATING COST SUMMARY
FIRST FULL YEAR OPERATION - M\$/YR

		<u>SNG ONLY</u>	<u>SNG/MeOH</u>
Coal Supply		49,425(1)	54,733(2)
Catalyst & Chemicals		3,366	4,936
Wages & Salaries		7,976	8,360
G&A @ 25%		1,994	2,090
Maintenance Materials		4,830	5,062
Supplies		6,370	6,400
Ash Disposal		500	500
Taxes & Insurance		5,880	6,618
Water Supply		<u>415</u>	<u>501</u>
		80,756	89,200
<u>BY-PRODUCT CREDITS</u>			
Sulfur	78,110 T @ \$20/T	1,562	1,562
Crude Phenols	41,610 T @ \$50/T	2,081	2,081
Naphtha	56,794 T @ \$67/T (\$9/bbl)	3,805	3,805
Tars	339,085 T @ \$30/T	10,173	10,173
Fuel Oil	112,347 T @ \$67/T (\$9/bbl)	7,527	7,527
Ammonia	65,700 T @ \$85.7/T	<u>5,629</u>	<u>5,629</u>
		30,777	30,777
NET		49,979	58,461

NOTES:

1. 164.751 M⁴Btu/Y @ \$.30/M²Btu
2. 182.444 M⁴Btu/Y @ \$.30/M²Btu

ECONOMICS - EQUAL PRICE/BTU BASIS

	REQUIRED SALES PRICE (\$/MMBtu) 25-Year Average	
	<u>SNG PRODUCTION</u>	<u>SNG/MeOH CO-PRODUCTION</u>
30¢/M ² Btu Coal Feed	1.94	2.12
60¢/M ² Btu Coal Feed	2.52	2.73
90¢/M ² Btu Coal Feed	3.09	3.34

SENSITIVITY FACTORS

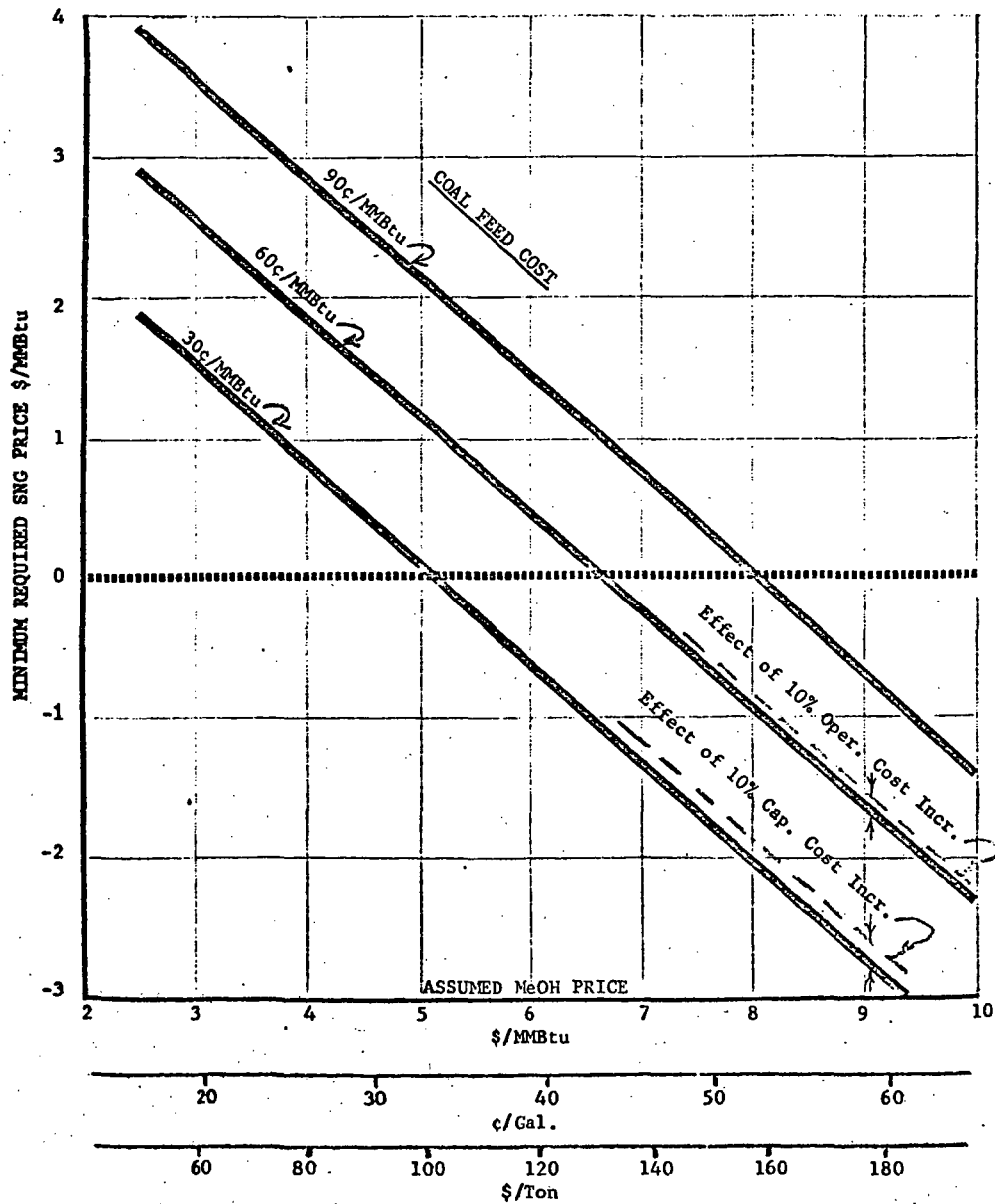
I. 10% Capital Investment Increment -	<u>SALES PRICE INCREMENT</u>
	.16
II. 10% Yearly Operating Cost Increment -	<u>SALES PRICE INCREMENT</u>
	.05

SNG SALES PRICE AT VARIOUS MeOH SALES PRICES

<u>ASSUMED MeOH SALES PRICE</u>		<u>MINIMUM REQUIRED SNG SALE PRICE</u>		
<u>¢/Gallon</u>	<u>\$/MMBtu</u>	<u>30¢/M²Btu Coal Feed</u>	<u>60¢/M²Btu Coal Feed</u>	<u>90¢/M²Btu Coal Feed</u>
		<u>\$/MMBtu</u>		
16.2	2.50	1.85*	2.89	3.92
19.4	3.00	1.51	2.54	3.58
22.7	3.50	1.16	2.19	3.23
25.9	4.00	0.81	1.84	2.88
29.2	4.50	0.46	1.49	2.53
32.4	5.00	0.11	1.15	2.18
35.6	5.50	Negative	0.80	1.83
38.9	6.00	Negative	0.45	1.48
42.1	6.50	Negative	0.10	1.13
45.4	7.00	Negative	Negative	0.79
48.6	7.50	Negative	Negative	0.44
51.8	8.00	Negative	Negative	0.09
55.1	8.50	Negative	Negative	Negative
58.3	9.00	Negative	Negative	Negative
61.6	9.50	Negative	Negative	Negative
64.8	10.00	Negative	Negative	Negative

*Range where co-produced SNG sales price falls below sales price of SNG produced alone.

MINIMUM REQUIRED SNG PRICE
AT VARIOUS MeOH PRICES



UTILITY ENERGY REQUIREMENTS
REPLACEMENT BY CLEAN LIQUID FUELS (METHANOL, NGL)

User	Equipment	Gas MMcf/Day	Methanol Tons/Day
Texas and Louisiana electric utilities	Boilers not requiring conversion	115	5,900
	Boilers requiring conversion	3,450	177,000
	Gas turbines in Texas and Louisiana	44	2,260
Transco customers	Public Service Electric Company's gas turbines (estimate)	55	2,800
	Consolidated Edison Company's gas turbines (1973)	52	2,660
Transco pipeline	Compressors @ 1 trillion CF/yr. delivery	123	6,300

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CAS
7/26/74

TOTAL U. S. PEAKING FUEL REQUIREMENT
ELECTRIC GENERATING UTILITY INDUSTRY
GAS TURBINES & INTERNAL COMBUSTION ENGINES

<u>Type of Fuel</u>	<u>Fuel Consumption April 1974 (FPC)</u>	<u>Methanol Equivalent</u>
Gas	624,500 Mcf/D	32,000 T/D
Fuel Oil (Distillate)	210,540 Bbls/D	62,800 T/D

THE FISCHER-TROPSCH PROCESS: GASOLINE FROM COAL

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INTRODUCTION

The Federal Bureau of Mines was engaged from 1944 to about 1969 in a research and development program on the synthesis of gasoline and other Fischer Tropsch products from coal. The actual Fischer Tropsch reactor designs and catalyst work was done at Bruceton in what is now the Pittsburgh Energy Research Center of the U. S. Energy Research and Development Administration.

Historically the work was covered extensively by Storch.⁽¹⁾ This paper will cover the work done at Bruceton in the 1944-1969 period and the development of the various reactors and catalysts plus the present work.

OIL CIRCULATION PROCESS

The oil-circulation process was developed at Bruceton for synthesizing liquid fuels by the Fischer-Tropsch reaction.⁽²⁾⁽³⁾ Carbon monoxide and hydrogen react over an iron catalyst to produce a product that is essentially hydrocarbons ranging from methane to high molecular weight wax. Removal of the heat of reaction (50,000 Btu/gallon of liquid product) is achieved by sensible heating of a recycle oil that completely covers the catalyst.

Although granular fused iron oxide (synthetic ammonia catalysts) used as a fixed-bed was active as a catalyst, gradual cementation of the particles together caused increased pressure drop. This problem was alleviated by operating with an expanded bed.⁽⁴⁾ Because attrition caused gradual disintegration of the catalyst, catalysts with an inert core of iron and an external coating of catalytically active iron were developed such as oxidized ironshot. These experiments finally led to the development of lathe-turnings catalyst. This catalyst was used in a fixed-bed and showed no attrition problem, and the large void volume eliminated the problem of cementation. Table 1 shows data taken from this type of operation.

HOT GAS RECYCLE

The oil circulation system was limited in temperature and the hourly space velocity (SVH). The temperature could not be raised above 300° C without cracking and volatilizing the oil. The SVH could not be raised much above 800 without lowering the gas conversion. To overcome these problems, we turned to the hot-gas-recycle process.⁽⁵⁾ This process uses a fixed bed of catalyst (lathe-turnings), through which large volumes of recycle gas are circulated to remove the heat of reaction as sensible heat. The lathe-turnings incurred a low pressure drop (about one psi/ft of bed height). Table 2 shows the results of several tests and shows the effects of some process variables on product distribution.

The parallel plate type catalyst was developed as a variant of the lathe-turning catalyst used in the hot-gas-recycle work. The pressure drop across this catalyst was significantly lower than that of the lathe-turning catalyst.⁽⁶⁾

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TABLE 1. - Typical experimental conditions and hydrocarbon yields in experiment 37 using steel lathe-turning catalyst in the oil-circulation process

Test period:	14	15	16
Catalyst age.....hr	1,503-1,527	1,551-1,671	1,671-1,791
Hourly space velocity of fresh gas.....hr ⁻¹	700	601	600
Space weight velocity, ft ³ (STP)/hr-lb Fe.....	8.74	7.51	7.51
Maximum pressure.....psig	310	312	313
Pressure differential.....psi	10	10	10
Maximum temperature.....°C	290	290	290
Temperature differential.....°C	7	6	6
Recycle-to-fresh gas ratio.....	2:1	2:1	2:1
CO ₂ scrubbing.....	Yes	Yes	Yes
Synthesis gas ratio.....H ₂ :CO	1.018	1.014	1.025
Usage ratio.....H ₂ :CO	0.849	0.869	0.855
CO ₂ -free contraction....volume-percent	65.1	63.6	57.8
H ₂ conversion.....do.....	63.7	63.1	56.8
H ₂ +CO conversion.....do.....	70.0	68.3	62.3
CO conversion.....do.....	76.4	73.6	68.0
Ft ³ H ₂ +CO converted/lb Fe.....	6.12	5.13	4.68
Yields, g/m ³ H ₂ +CO converted:			
C ₁	15.4	20.3	21.4
C ₂	3.9	4.0	4.3
C ₂	18.2	16.1	14.2
C ₃	7.4	9.4	10.2
C ₃	7.8	8.9	6.6
C ₄	13.7	14.9	14.4
C ₄	3.4	6.4	9.5
C ₅	13.2	12.8	10.7
C ₅	3.4	2.4	3.7
C ₆	6.0	4.3	3.8
C ₆	(1)	(1)	(1)
Light oil.....	68.9	61.9	62.4
Heavy oil.....	2.5	12.9	7.9
Aqueous layer.....	67.9	69.2	68.5
Product recoveries, lb/day:			
<204° C.....	18.24	15.88	14.71
204-316° C.....	4.11	3.00	2.89
316-450° C.....	1.92	1.71	1.63
>450° C.....	0.97	1.14	1.09
Product distribution, weight-percent:			
<204° C.....	72.3	73.0	72.4
204-316° C.....	16.3	13.8	14.2
316-450° C.....	7.6	7.9	8.0
>450° C.....	3.8	5.3	5.4
Relative catalyst activity ²	87	72	61
Recovery.....weight-percent	100.2	101.2	101.3

¹None detected.

²Anderson, R. B., and others, Ind. and Eng. Chem., v. 44, 1952, pp. 391-397.

TABLE 2. - Effect of variables on product distribution¹

Experiment and period	Reactor temperature change	Fresh gas		Hourly space velocity	Percent water in recycle gas		Percent CO ₂ in recycle gas		Chlorine deposition on catalyst		Potassium impregnation	
		11-A 11-B	16-D 16-F		8-H 8-K	7-D 7-E	7-F 7-G	7-J 7-K	13-A 13-B	8-C 8-D	9-C 9-D	
Recycle to fresh feed ratio:												
Total	162 81	17	16	60	67	65	60	60	44	35	105	108
Cold	2.6 2.8	2.6	4.5	2.8	2.9	67	2.5	2.5	0	2.2	2.2	3.0
Average reactor temperature.....° C.												
CO ₂ in recycle gas	353 390	305	313	300	329	305	310	319	319	319	303	315
Water in recycle gas	4.8 5.0	5.0	2.4	10.1	10.1	6.4	4.9	5.3	29.8	5.3	1.6	4.6
Space velocity	-	4.3	4.9	4.1	4.0	0.2	2.5	5.0	7.3	5.1	7.3	3.4
Space velocity	265 244	1,001	1,000	1,003	1,400	400	400	600	600	799	800	400
H ₂ :CO ratio:												
Fresh gas	1.41 1.23	1.36	2.91	1.29	1.30	1.28	1.31	1.29	1.29	1.40	1.46	1.28
Usage	0.96 1.02	1.26	2.61	1.16	1.15	1.21	0.97	1.09	0.73	1.13	1.73	1.16
Recycle	4.32 3.58	10.0	22.4	6.51	4.03	1.50	3.21	8.04	7.68	8.31	0.88	4.33
Weight-percent of hydrocarbons:												
C ₁ +C ₂	30.1 48.3	47.3	59.5	33.9	32.1	17.3	25.7	19.5	24.9	25.6	18.8	38.0
C ₃	4.2 6.8	16.5	17.5	13.0	11.2	0.5	1.3	3.1	3.7	3.3	2.5	15.2
Gasoline (C ₃ = - 204° C)	46.4 42.1	35.5	23.0	45.8	50.6	48.9	49.5	58.1	59.8	57.7	66.2	39.4
Diesel oil (204°-316° C)	7.1 2.5	0.7	0	6.8	5.8	13.0	10.2	11.3	6.7	6.7	7.7	3.6
Fuel oil + wax (316° C +)	12.2 0.3	0	0	0.4	0.3	20.3	13.3	7.4	4.9	6.7	4.8	3.8
Specific yield, g/m ³ H ₂ +CO converted:												
Oxygenates	8.8 7.5	2.5	3.8	5.9	5.4	10.8	8.1	9.6	6.2	9.0	2.6	3.3
C ₂ -C ₆ olefins	41.3 37.5	10.7	7.5	18.1	31.6	28.5	34.6	39.0	74.4	41.3	51.5	16.9
Potassium oxide content on catalyst	-	-	-	-	-	-	-	-	-	-	0.04	0.16
Chlorine content on catalyst	-	-	-	-	-	-	-	-	-	-	20.002	30.05

¹Underlined figures indicate change in variable.

²Chlorine content of oxidized and impregnated turnings similar to that used in experiment 13.

³Chlorine content of the discharged catalyst.

In this system catalysts are flame sprayed onto plates which then are assembled into parallel plate modules (figure 1) and stacked in the reactor. Originally a coating of synthetic ammonia catalyst (SAC) was used, but the most recent work used Alan Wood magnetite (AWM) impregnated with K_2CO_3 . (7) Table 3 shows data from this work (Ex. 34) plus an experiment using the SAC (Ex. 33). Note the 2000 SVH achieved in the latest experiment and the greater proportion of gasoline-range hydrocarbons. This SVH is an economical feed rate considering the number of reactors necessary for a commercial plant.

SLURRY EXPERIMENTS

At the same time that the oil circulation system was being developed considerable work was proceeding on oil slurry operations. (8) In the slurry process, a finely divided fused iron catalyst (less than 5 microns) is kept in suspension in an oil (paraffin oil--b.p. less than 384°C) by the agitation of synthesis gas rising through the slurry. In some of the experiments a new type catalyst, a nitrided iron catalyst, was used to attempt to maximize the yield of oxygenates, especially alcohols. Table 4 shows such data comparing the results of a test of the nitrided with the fused iron catalyst.

FLUIDIZED-BED TESTS

A series of tests were performed in a fluidized-bed also using a nitrided, fused iron catalyst. (9) The reactor was a 1-inch ss pipe, 6 feet long, enclosed in a 3-inch heat exchanger jacket. About 78 percent of the $\text{H}_2:\text{CO}$ fresh feed was converted when the unit was operated at a SVH of 750, a 8:1 recycle-to-fresh feed gas ratio, a 300 psig pressure and a temperature of 252°C . About 33 percent of the total hydrocarbons made were oxygenates.

PRESENT WORK

Our present work in F.T. synthesis is based on the hypothesis that, because of the great change in the energy picture in the U. S., variations of the Fischer-Tropsch reaction may be economically viable. Cost studies (10) indicate that a modified SYNTHANE (11) coal-to-gas system where a Fischer-Tropsch reactor is substituted for the methanation reactor and the H_2/CO ratio of the raw SYNTHANE gas is utilized, will yield a combination of substitute natural gas and light oil at minimum cost.

While the aim of the program at PERC is to use the Hot-Gas-Recycle pilot plant (with catalyst sprayed on parallel plates), the first experiment is being done in a bench-scale tube-wall reactor system. Figure 2 shows this reactor system and figure 3 a photo of an actual sprayed section.

The tube was a 3/4-inch stainless steel tube flame sprayed with a 0.020-inch coating of AWM; the coating was six inches in length. The magnetite was reduced with H_2 at 400°C . Then synthesis gas ($3\text{H}_2 + \text{CO}$) was introduced. Conditions of operation were: 1000 psig pressure and $310\text{--}315^\circ\text{C}$; flow rate was 4.37 scfh, equivalent to 1640 SVH (based on the annulus volume), or 30 scfh per sq. ft. of catalyst area, a more meaningful term for this type of operation. The heat of reaction was removed from the catalyst surface by boiling Dowtherm on the inside of the tube. Results of the first test are shown in table 5 where we operated at 300, 650 and 1000 psig.

Table 5 shows an increase in the $\text{C}_1\text{--C}_4$ alcohols with increasing pressure. The yield of hydrocarbons was low, as expected, because of the increased throughput (as given as scfh feed gas/ ft^2 catalyst area). This also favored the formation of lighter hydrocarbons as shown in the wt-pct of the various hydrocarbon streams.

Planned tests include tests with Raney Iron before changing the H_2/CO ratio in the feed gas.

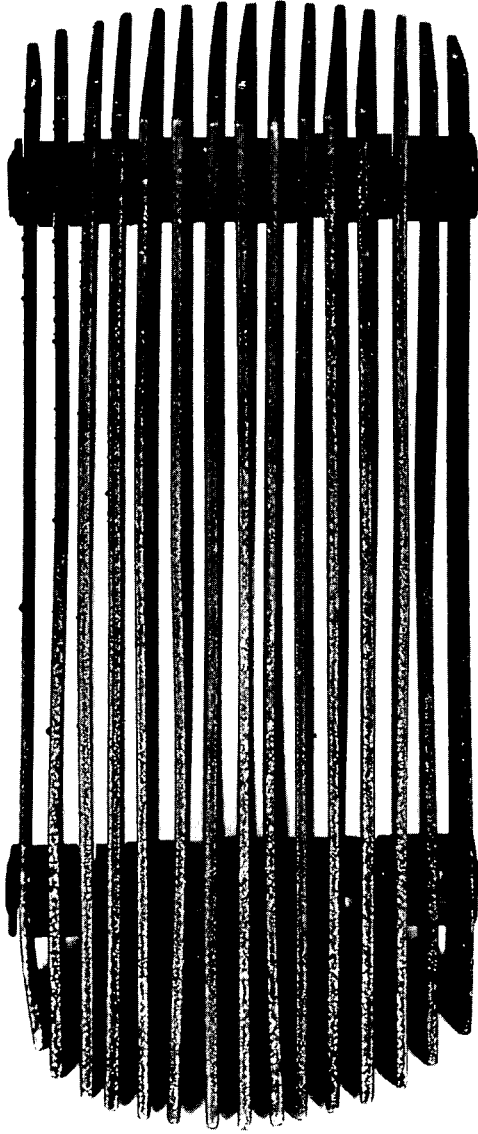


TABLE 3. - Hot-gas recycle synthesis results with flame-sprayed catalyst-coated plate assemblies

	Exp. No. HGR 33		Exp. No. HGR 34	
Fresh gas space velocity, vol/vol hr.....	600	1000	1000	2000
Total recycle in fresh feed, vol/vol.....	52	15.9	20.4	14.4
Reactor pressure, psig.....	400	400	400	400
Catalyst temperature, °C				
Average.....	269	325	320	325
Differential.....	20	50	40	50
H ₂ conversion, pct.....	73.4	90.9	90.1	83
CO conversion, pct.....	80.6	98.8	98.2	94.4
H ₂ +CO conversion, pct.....	76.4	94.4	93.4	87.5
Overall weight balance, pct.....	93.6	90.8	87.8	96.6
Hydrocarbons recovered, lb/1000 SCF fresh gas.....	7.4	9.5	10.3	11.6
Hydrocarbons recovered, wt-pct				
C ₁ +C ₂	59.7	36.5	33.9	29.5
C ₃	6.6	14.1	13.3	12.8
Gasoline (C ₃ = <240° C.....	31.8	43.7	48.5	53.0
Diesel oil (204°-316°C).....	1.9	5.0	4.0	3.8
Fuel oil (316°-450° C).....	0	0.4	0.2	0.5
Wax (>450° C).....	0	0.3	0.1	0.4

TABLE 4. - Slurry Test Data

Experiment No.....	LP-99	LP-66
Catalyst.....	Fused Iron	Nitrided Fused Iron
Space Velocity, scfh/ft ³ volume.....	300	300
Temperature.....	255° C	250° C
H ₂ +CO Conversion, pct.....	69.7	46.6
Usage Ratio.....	1.02	0.84
Yield gm/m ³ (H ₂ +CO) Converted:		
C ₁ -C ₂	20.0	44.4
Gas C ₃ -C ₆	39.2	67.4
Light Oil.....	78.8	55.4
Heavy Oil.....	47.3	0.0
Aqueous Layer.....	90.5	65.0
Yield C ₃ ⁺	165.3	154.1
Oxygenates.....	6.9	44.9
Infrared Analysis of		
Light Oil, wt-pct:		
OH.....	2.1	10.9
COOH, COO, CO.....	1.2	1.8
C=C.....	10.21	5.3
Aqueous Product:		
Oxygenated Compounds:		
(KFR) wt-pct.....	4.3	58.2

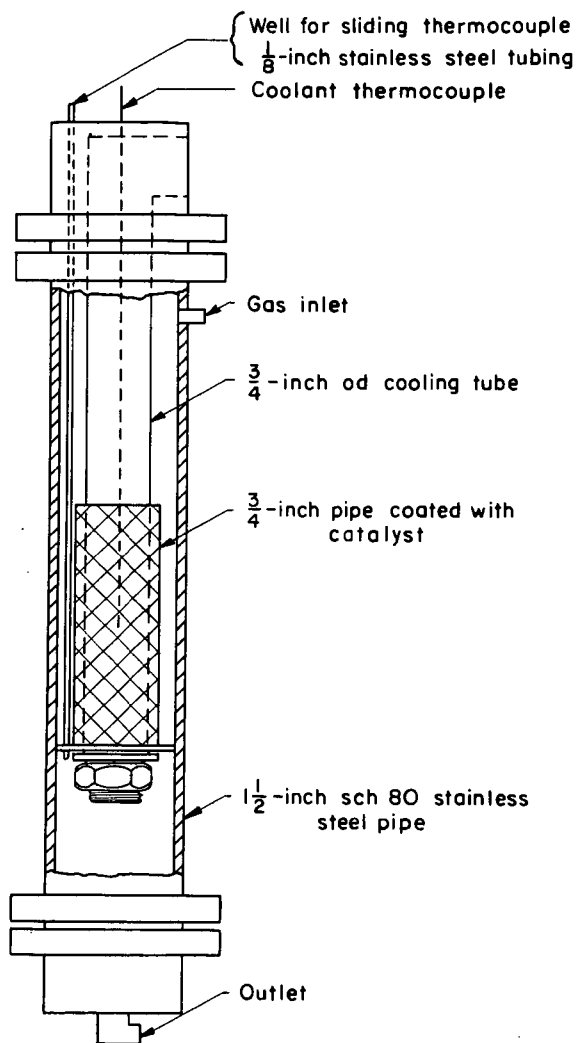




TABLE 5. - Results of bench-scale F.T. test compared to HGR-34

Experiment Number	HGR-34			FT-TW-1		
Fresh gas $\frac{\text{vol. gas, ft}^3/\text{hr}}{\text{Ft}^2 \text{ catalyst surface}}$	8.85	17.7	30	30	30	
H ₂ /CO ratio in feed gas	1.4/1	1.4/1	3/1	3/1	3/1	
Reactor pressure, psig	400	400	300	650	1,000	
Catalyst temp. average °F/°C	608/320	617/325	615.2/324	602.6/317	609.9/318	
H ₂ Conversion, percent	90.1	83	40.32	43.67	45.12	
CO Conversion, percent	98.2	94.4	78.30	78.46	76.21	
H ₂ + CO Conversion, percent	93.4	87.5	49.38	52.02	52.70	
Heating value tail gas Btu/ft ³						
With CO ₂	930	785	383	408	418	
Without CO ₂	1,000	852	419	447	453	
Overall weight balance, percent	87.8	96.6	93.96	97.05	95.72	
Hydrocarbons recovered lb/1000 scf fresh gas ^{1/}	10.3	11.6	4.148	5.139	5.714	
Theoretical hydrocarbons, g/m ³ (H ₂ + CO) conversion	190.28	197.0	188.65	184.13	166.98	
Recovery, percent	119.53	97.39	71.33	82.76	108.09	
Hydrocarbon recovered, wt-pct.						
C ₁ + C ₂	38.00	32.71	71.26	67.01	69.56	
C ₃	13.58	12.07	17.70	19.92	11.75	
Gasoline (C ₃ ^m + <204°C) ^{1/}	48.11	50.01	9.18	12.14	18.32	
Diesel Fuel (204° C- 316°C)	4.46	4.27	1.60	.83	.32	
Fuel Oil (316°C-450°C)	.18	.52	.25	.10	.06	
Wax (>450° C)	.11	.42	0.0	0.00	0.00	
			Period			
Aqueous layer, grams/m ³ (H ₂ + CO) Conv.			1st	2nd	1st	2nd
C ₁ -C ₄ OH			3.16	4.34	7.70	17.14
Other oxygenates			.19	.13	.13	.18
H ₂ O			126.7	124.9	140.6	135.2
Percent CO in tail gas			8.09		8.0	

^{1/}Includes alcohols and oxygenates.

CONCLUSION

We believe more work in the area of the Fischer-Tropsch reaction is needed. The process is very flexible; most any desired product can be obtained by selected reactor type, catalyst, operating temperature and synthesis gas ratio. Operating conditions can be easily changed to maximize the yield of product most in demand at any given time. Our work will continue to stress primarily the gasoline yield but oxygenates could be a desired byproduct.

REFERENCES

1. Storch, H. H., N. Golumbic, and R. B. Andersen. The Fischer-Tropsch and Related Syntheses: John Wiley and Sons Inc., New York, N.Y., 1951, 610 pp.
2. Bienstock, D., A. J. Forney and J. A. Field. Fischer-Tropsch Oil-Circulation Process. Experiments With A Massive-Iron Catalyst. RI 6194, 1963, 20 pp.
3. Bienstock, D., J. H. Field, A. J. Forney, J. G. Myers and H. E. Benson. The Fischer-Tropsch Synthesis In the Oil Circulation Process: Experiments With A Nitrided Fused-Iron Catalyst. RI 5603, 1960, 32 pp.
4. Rensen, H. E., J. H. Field, D. Bienstock, R. R. Nagle, L. W. Brunn C. O. Hawk, J. H. Crowell and H. H. Storch. Development of the Fischer-Tropsch Oil Recycle Process. BuMines Bull. 568, 1957, 72 pp.
5. Field, J. H., D. Bienstock, A. J. Forney and R. J. Demski. Further Studies of the Fischer-Tropsch Synthesis Using Gas Recycle Cooling (Hot-Gas-Recycle Process). RI 5871, 1961, 32 pp.
6. Forney, A. J., R. J. Demski, D. Bienstock and J. H. Field. Recent Catalyst Developments in the Hot-Gas-Recycle Process. RI 6609, 1965, 32 pp.
7. Elliott, J. J., W. P. Haynes and A. J. Forney. Gasoline Via the Fischer-Tropsch Reactor Using the Hot-Gas-Recycle System. Reprint 163rd National Meeting of ACS, Boston, Mass., Fuels Division, vol. 16, No. 1, April 1972, pp. 44-50.
8. Schlesinger, M. D., H. E. Bensen, E. M. Murphy and H. H. Storch. Chemicals From the Fischer-Tropsch Synthesis. Industrial and Eng. Chemistry, vol. 46, June 1954, pp. 1322-1326.
9. Demeter, J. J. and M. D. Schlesinger. Fischer-Tropsch Synthesis in a Fluidized-Catalyst Reactor with a Nitrided Fused-Iron Catalyst. RI 5456, 1959, 16 pp.
- 10.1 Katell, Sidney, and staff. A Combined SYNTHANE Gasification of Montana Coal at 1000 psi and Fischer-Tropsch Synthesis to Produce High-Btu Gas and Liquid Products. Report 74-21, Jan. 1974, 63 pp.
11. Forney, A. J. and J. P. McGee. The SYNTHANE Process--Research Results and Prototype Plant Design. Fourth AGA Synthetic Pipeline Gas Symposium, Chicago, Ill., Oct. 1972, pp. 51-72.

COAL GASIFICATION AT THE BELLE WORKS

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EARLY YEARS AND PROCESS DEVELOPMENT

In August 1924, Slack's Farm in Belle, West Virginia was chosen as the site for an ammonia plant to be operated by L'Azote Inc., a subsidiary of E. I. du Pont de Nemours Inc. The site was selected because of the availability of bituminous coal from the West Virginia and Pennsylvania fields. Plant operations began in April 1926 when synthetic ammonia was produced by the Claude process at a thousand atmospheres. Coal was gasified with steam producing "Blue Gas" as shown in Equation 1. The actual "Blue Gas" contained in addition to CO and H₂ small amounts of CO₂, N₂, methane and sulfur compounds. The "Blue Gas" was liquefied and purified to yield hydrogen, which was burned with air to obtain a mixed gas for ammonia synthesis.



Because of difficulties associated with coal caking during gasification, the process was modified in 1930 to make coke and then gasify the coke. A battery of 46 coke ovens was installed and coke was gasified with steam and air in cyclic gas generators producing "Blue Gas" and "Blow Run Gas." In addition, coke oven gas was processed to recover coal tar byproducts; methane and carbon monoxide were removed by liquefaction; and hydrogen was recovered. The methane, carbon monoxide stream was returned as fuel to the coke ovens. At about the same time commercial methanol synthesis was begun at Belle with the "Blue Gas" being used mainly for methanol and carbon monoxide manufacture while the "Blow Run Gas," which contained nitrogen, was used for ammonia synthesis. During the 1930's and '40's, production was begun on a number of other products based on carbon monoxide, hydrogen, methanol and ammonia. Among these were nylon intermediates, methyl methacrylate, urea and ethylene glycol.

In 1948, the gasification of coke with steam and oxygen on a continuous basis was started in three of the cyclic generator sets. Elimination of nitrogen made it possible to produce "Blue Gas" continuously. Meanwhile, information about German work on partial oxidation of coal to produce carbon monoxide and hydrogen for Fischer-Tropsch synthesis helped to stimulate laboratory work on partial oxidation processes leading to a semi-works scale unit at Belle which operated in 1948-49. A view of this unit is shown in Figure 1. It was an entrained feed, atmospheric pressure process which ran a total of 1200 hours with the two longest runs being of 65 and 66 hours duration. It used 120 tons of several coals and consumed 111 tons of oxygen during its operation.

Growing out of the semi-works experience, a pilot plant was designed and started in 1950, see Figure 11. Operation of the pilot plant was successful in demonstrating the general feasibility of the coal partial combustion process in larger scale equipment. Satisfactory gas production rates and coal, oxygen, and steam consumption rates were achieved indicating substantial economies over coke gasification. Further process improvement was needed in slag removal and increased gas yield by reduction of ungasified carbon.

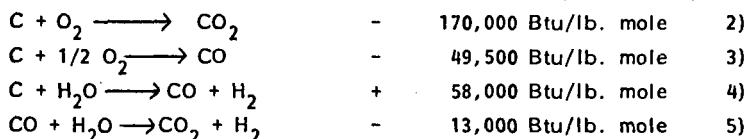
A similar program was followed by Babcock & Wilcox and resulted in a pilot unit at the Bureau of Mines' station at Morgantown, WV⁽¹⁾. The Babcock & Wilcox gasifier also used steam to entrain the pulverized coal but

was designed for up-flow in the generator. In October 1951 a Babcock & Wilcox designed generator was installed and operated in the Belle pilot plant. The experience gained from the total pilot plant operation led to a collaboration between Babcock & Wilcox and Du Pont in the design and installation of a commercial scale coal partial oxidation unit at Belle in 1955.

COMMERCIAL SCALE OPERATION

Process Description

The coal partial combustion process is based upon the gasification of pulverized coal in suspension with oxygen and steam. Gasification takes place by several reactions which occur simultaneously. The heats of reaction are given at 2200°F, although the reaction zone temperature was approximately 500°F higher.



As coal entered the generator mixed with steam and oxygen it rapidly devolatilized and reacted to produce CO_2 , CO and H_2 . These products of combustion and gasification then reached equilibrium with respect to the shift reaction, Equation 5.

At the high generator temperature the ash in the coal melted and was deposited in the generator base where it drained from the reaction zone. Some small particles of ash were carried along with the main gas stream and passed out of the reaction zone along with the ungasified carbon. The molten slag from the bottom of the generator fell into a pool of water where it fractured and was removed by a lock hopper and slag pump.

The residence time of the gas in the reaction zone was approximately 1.4 seconds. Residence time for fine coal particles was probably about the same, although for the larger particles the time would be greater since they would tend to fall back to the bottom.

From the reaction zone the gases passed through a heat removal zone where 465 psig steam was produced, the boiler feed water being preheated in an economizer. Ash and ungasified carbon were removed by water washing using orifice and plate scrubbers. This wash water was sent to a clarifier before being discharged. The sludge was pumped away and used as fill along with boiler fly ash.

In the generator there was approximately 1 mole of water for every 3 moles of product gas. Sulfur in the coal was converted predominantly to hydrogen sulfide; a typical H_2S concentration was 0.2%.

Equipment Description

Coal Feeding

From a silo, crushed coal was weighed and discharged into a hopper. A screw conveyor to control the feed rate discharged into a star seal which was blanketed by CO_2 . A second screw conveyor carried the coal into a steam jet pulverizer where it was pulverized to 90% through a 325-mesh screen with 145 psig steam. Oversized particles from the pulverizer were removed by a spinner classifier. Pressure at this point was 125 inches of water. Coal was conveyed by steam from the pulverizer to the generator.

Just before the generator, 95% oxygen at 250 inches of water pressure was added to the coal-steam stream. Velocities and distribution of the pulverized coal in the steam-oxygen gas mixture were critical to avoid flashback from the generator to the point of oxygen addition. Figure III illustrates the coal pulverizer feeder and its operation.

Generator

The generator itself was a refractory lined vessel with the gasification zone 30 feet high by 11.4 feet i.d. The refractory lining consisted of a 9-inch thick 15-foot high cast alumina section backed up by two layers of insulating brick, one 9 inches thick and the other 4-1/2 inches thick. This refractory construction was inside a water tube wall which was part of the steam boiler. There was a containment shell outside of this wall, see Figure IV. The water tubes supported the refractories from the bottom and the entire generator was suspended from overhead beams; as it expanded it elongated downward. There were two 16-inch downcomers to circulate water through the tubes to the boiler on top. The generator floor was made by bending every other water tube inward toward the slag tap hole which was above the floor so a 9-inch pool of slag existed in the generator. The hole was formed by a pipe coil in a cone shape to give an 8-1/2-inch opening.

Ports were provided for temperature measurements near the burners and at numerous other points. Thermocouples were imbedded in the refractories. There were four water cooled coal burners, so arranged that two could operate at a time, but only 180° apart. These were directed downward toward the slag top opening to assist in keeping the ash molten. Velocity through the burners was 125 ft./sec.

Boiler

Gases leaving the reaction zone passed first through slag screen tubes, and then over the superheater tubes before passing over the boiler tubes. Soot blowers were positioned in the superheater and boiler tube sections to remove ash accumulations. Steam was generated at 465 psig and superheated to 780°F for use in turbines.

Gas Scrubbers

Following the boiler tubes, the gas passed through the economizer and then through an orifice scrubber, a wet cyclone, and a washer cooler before going to the gas holder. The wash water from these operations was sent to a large clarifier which was 10 feet deep and 50 feet in diameter. Sludge was removed from the bottom and clear water was drawn off from the top through a sludge blanket which was formed by lighter particles.

Design Basis

Specifications for gas generation were based on the data in Table I.

TABLE I 185

DESIGN BASIS

Coal Analysis	Carbon	78.3%
	Hydrogen	5.4
	Oxygen	9.3
	Sulfur	0.8
	Nitrogen	1.6
	Ash	4.6
Ash Fusion Temperature	2400° - 2450°F	
Steam to Coal Ratio	0.8 lb./lb.	
100% Oxygen to Dry Coal Ratio	9.2 cf/lb.	
Generator Temperature:	2700°F	
Generator Pressure:	75 inches of water	
Steam Generation:	54,000 pph @ 780°F	
Coal Feed Rate:	30,700 pph	
Oxygen:	95% Oxygen, 5% Argon & Nitrogen	
Product Gas:	CO	40.4% (Mole % Dry Basis)
	H ₂	40.4
	CO ₂	16.0
	CH ₄	0.6
	Illuminants	0.3
	H ₂ S	0.2
	O ₂	0.2
	N ₂ +A	1.9
Production Rate:	22,500,000 cu.ft./day of CO + H ₂	

Process Performance

Performance of the unit compared to that projected from pilot plant data was essentially as predicted. This is shown in Table II.

TABLE II

PROCESS PERFORMANCE

<u>Item</u>	<u>Projected</u>	<u>Performance</u>
<u>Feed</u>		
cf of 100% oxygen/lb. carbon	12.1	12.2
lb. steam/lb. carbon	1.0	1.0
cf 100% oxygen/lb. dry coal	9.6	9.9
lb. steam/lb. dry coal	0.79	0.81
coal rate pph	30,700	30,000
<u>Product</u>		
lb. dry coal/Mcf (CO + H ₂)	33.8	32.2
cf 100% oxygen/Mcf (CO + H ₂)	325	324
% carbon gasified	90.3	94.8
dust leakage (grains/100 cf)	5	3
gas analysis (dry basis)		
CO	40.4%	41.0%
H ₂	40.4	38.0
CO ₂	16.0	16.5

Operating Utility

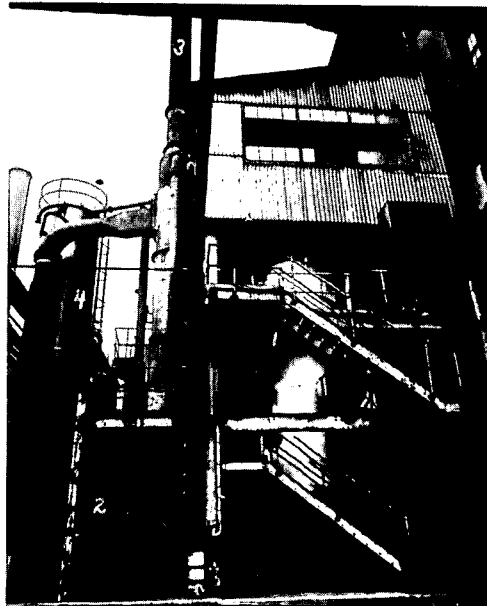
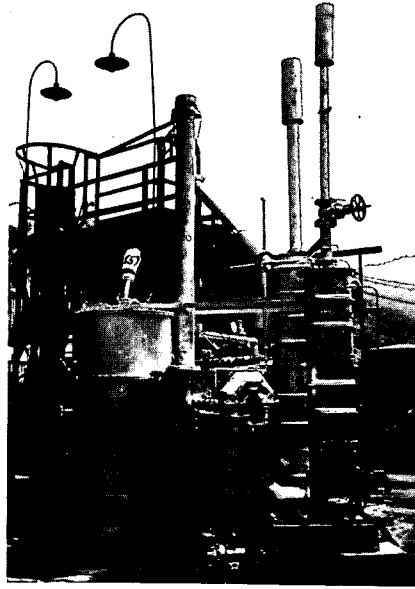
Operating utility of the unit was hampered by several mechanical difficulties. Beginning with the flow of materials through the unit, operation was interrupted by:

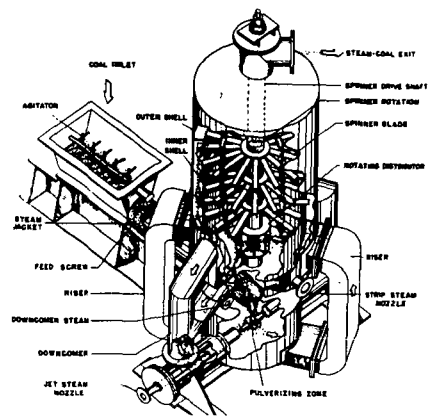
- Tramp material in the coal.
- Pulverized coal classifier shaft failure.
- Flashbacks of oxygen into burner.
- Refractory failures.
- Carbon and ash deposits in boiler.
- Superheater and boiler tube failures.
- Economizer tube failures.
- Stack valve expansion.

Figure V shows some of the refractory failure and Figure VI gives the overall picture of operating utility from startup in May of 1955 to August of 1956 when the unit was shut down and converted to partial combustion of natural gas. Actual operation of the commercial unit over this period totaled about 5,300 hours out of 11,250 hours or 47% of the time. Figure VII gives an impression of the size of this unit.

Literature Cited

- (1) P. R. Grossman and R. W. Curtis, "Pulverized-Coal-Fired Gasifier for Production of Carbon Monoxide and Hydrogen." Trans. ASMA Paper No. 53-A-49.





NOTE: Clockwise spinner rotation and facing of blades as shown are in error. Spinner rotation is actually counter-clockwise and facing of blades is reversed accordingly to same angle opening in direction of rotation.

FIGURE 1D1-13.01
1B3-3.01
PULVERIZATION
PULVERIZER-CLASSIFIER
AIRVIEW CUTAWAY

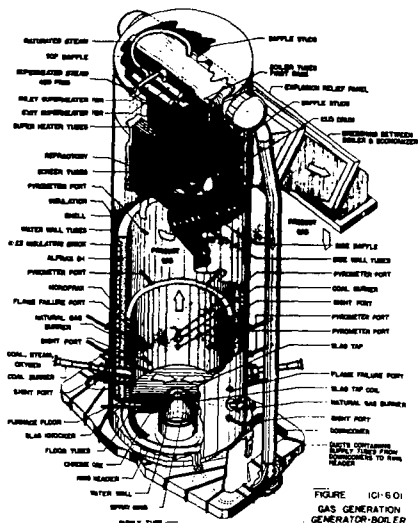
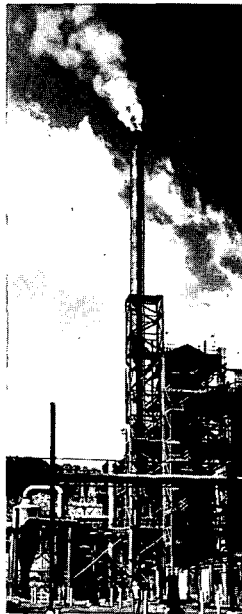
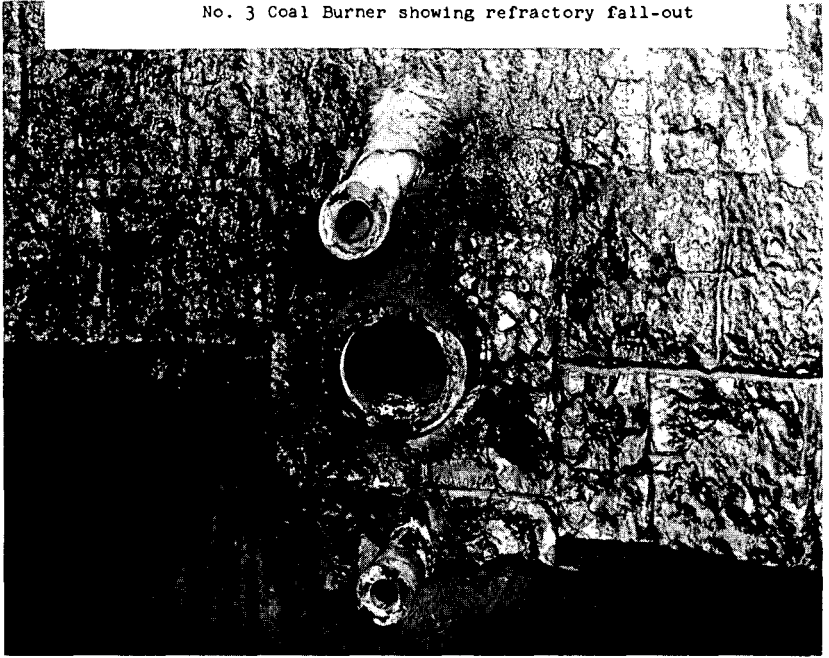
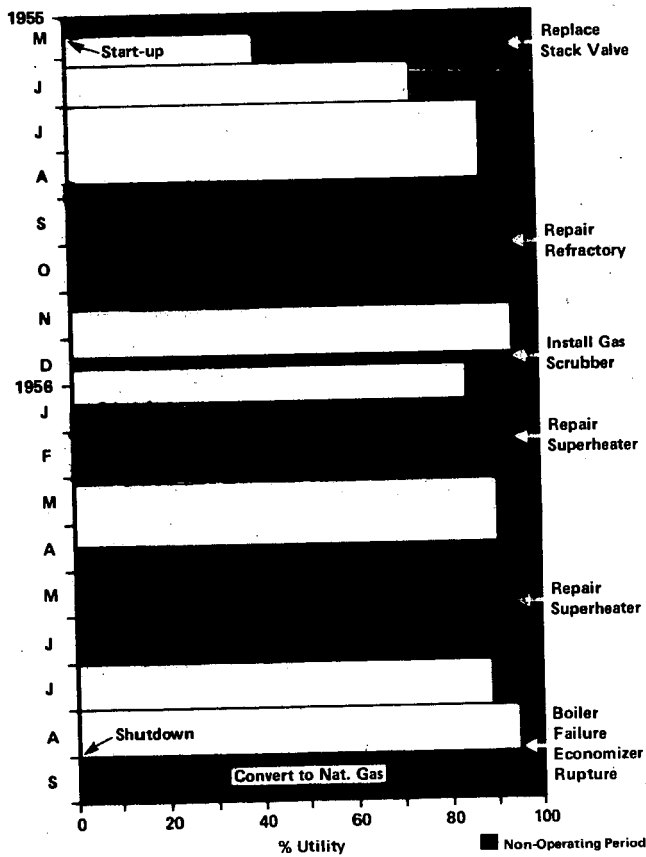


FIGURE 1C1-6.01
GAS GENERATION
GENERATOR-BOILER
AIRVIEW-CUTAWAY

No. 3 Coal Burner showing refractory fall-out



DU PONT B&W GASIFIER OPERATING UTILITY



METHANOL FROM COAL

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METHANOL FROM COAL

INTRODUCTION

Destructive distillation of wood originally provided the source of methanol alcohol. Other developments in the wood industry, namely plywood, for which nearly 40% of the production of methanol finds its way with forms of formaldehyde and associated resins have promoted its use and applications.

U.S. annual production in 1973 was close to one billion gallons or the equivalent of a 10,000 tons per day plant. The corresponding world production was 25,000 tons per day. By reason of its price and availability in recent years, natural gas was the preferred feedstock.

Some of the properties of methanol are given in Table 1.

Table 1 Properties and Other Data on Methanol

Composition	CH_3OH		
Appearance	Clear, colorless		
Density	.792		
Vapor Density	1.11		
Boiling Point	148°F		
Flash Point	52°F		
Ignition Temperature	800°F		
Explosive Limits (air)	Lower	6.0%	
	Upper	36.5%	
Calorific Values HHV	BTU	BTU	BTU
	per lb.	per gal.	per bbl.
Fuel Grade Methanol	9,760	64,771	2.72 million
No. 2 Fuel Oil	19,000	135,000	5.77 million
Western Coal-dry basis	10,345		

Conversion Factors:

$$\begin{aligned}
 1 \text{ Ton} &= 301.7 \text{ gal.} = 19.5\text{MM BTU} \\
 \$30.28 \text{ per ton} &- 10 \text{ c/gal.} = 1.54 \text{ \$/MM BTU}
 \end{aligned}$$

Recent developments have brought about a situation that gaseous feedstocks no longer prevail as a readily available raw material and alternative sources must be considered for the production of synthesis gas, coal being a strong contender.

The extent of the coal reserves has been compared by Linden¹ with other sources of energy and represents a substantial percentage of the recoverable fossil fuel reserves in the U.S.

Table 11

U.S. Fossil Fuel Reserves

	Proven & Currently Recoverable	Estimated Total Remaining Recoverable
Natural Gas	0.3 Q	1.5 Q
Natural Gas Liquids		0.1 Q
Crude Oil	0.2 Q	2.2 Q
Shale	0.4 Q	6.0 Q
Coal	4.3 Q	28.9 Q
Total	5.2	38.7

$$Q = 10^{18} \text{ BTU}$$

In items of heating value, coal represents 75 to 80 percent of these resources. At the current rate of consumption, 650 million tons per annum, these coal reserves can last well into the next century.

In comparison, a 5000 ton per day fuel grade methanol plant would consume about 4 million tons per annum of coal and give a daily output of about the equivalent of 90-95 MMSCFD of natural gas.

The applications of fuel grade methanol as alternate fuels have been reported extensively in the literature. Recent interest as a feed for gas turbines has been reported by Power & Marine Systems a subsidiary of United Technologies Corporation with tests at the St. Petersburg installation of Florida Power Corporation.

METHANOL FROM COAL

Historical Background

The price and availability of natural gas led to the early introduction in the U.S. of this material as a feedstock for the production of synthetic methanol. The conversion of the 30 ton per day plant in Peoria in 1932 to a methanol-from-natural gas unit was the forerunner of the industries transformation leading to plants up to the 2,000 tons per day range which have been in successful operation over the last few years.

Prior to the advent of natural gas, solid fuels had been the main sources of the raw material for the production of synthesis gas. In areas such as Europe, Asia and S. Africa where natural gas was not available, coal became established as the backbone of the ammonia and methanol industries and where suitable economics prevail these plants continue to operate. Recently a plant was commissioned in Modderfontein which manufactured both ammonia and methanol from coal. Hence, the technology is still available and can be readily updated to

suit U.S. conditions. Present designs incorporate the improvements which have evolved since the early 1920's when the plants first came into operations with high pressure synthesis processes.

The last unit to employ coal as a raw material for methanol synthesis in the U.S. was started up in Belle, W. Virginia using a B & W/DuPont oxygen blown gasifier and operated for about 15 months, gasifying approximately 400 T/D of coal to produce 24 MMSCFD of synthesis gas; about 1/3 of the output required for the 285 ton/day high pressure methanol facility that was in operation on that site.

Other installations that manufactured methanol from coal were located in Billingham Heysham and Dowlais in the United Kingdom (cyclic water-gas gassification with H.P. methanol). Leuna in E. Germany (Winkler gassification with H.P. methanol and Mayengibe Paris, France (Koppers-Totzek).

Methanol Synthesis

The growth of the synthetic methanol business from one million gallons per annum in 1927 to 80 million gallons per annum in 1947 has been described by Kastens, Dudley and Troeltzsch⁴.

Recent interest in methanol as an alternate fuel has resulted in a number of conferences and papers. A critical analysis of these latest developments was given by McGhee⁵ at the Engineering Foundation Conference in New Hampshire in July 1974. Whilst emphasizing the reduction in energy requirements from 4 to 2 BTU per BTU of methanol, his paper contains a useful bibliography on the new low pressure 50/100 atm process, as compared to the high pressure up to 1,000 atm processes.

The amount of natural gas being flared was mentioned by Harrison⁵ in a recent symposium on synthetic fuels. This gas could be utilized as part of a concept of transporting energy in the form of fuel grade methanol as opposed to LNG and it has been demonstrated that designs of units of 5,000 tons per day capacity are perfectly feasible and incorporate features of plants already in existence. In addition, checks with equipment suppliers indicate that such items as the methanol converter can be manufactured in the sizes required for a jumbo methanol unit.

Schemes have been proposed for up to 25,000 tons per day of methanol (corresponding to 480 billion BTU/day of product). These should be compared with the coal to SNG projects based on western coals which have normal capacities of 250 billion BTU/day of pipeline quality gas at 1,000 psi.

Later in this paper we will touch briefly on the economics of these large size units and the change in emphasis in capital investment which is about 20% for methanol synthesis in a coal based unit compared with about 40% in a gas based unit.

Coal Gasification

Early gasification processes date back to the last century; for example in 1883 Ludwig Mond designed a producer gas unit employing air as the gasifying medium for 200 tons/day of coal. This type of unit became the forerunner for the semi-water gas plant designed to produce synthesis gas at low pressure to feed the Haber process for ammonia which went into operation in Germany at Oppau in 1913. Synthetic methanol was first produced on the industrial scale by BASF in Germany in 1923. Coke from gas ovens often was the most popular feedstock for these cyclic plants of which well over 1,000 units were put in operation.

Gasification of inferior fuels such as brown coals and lignite developed with the invention of the fluidized bed Winkler process in 1926 which also had the advantage of being a continuous process. To date, there have been built 36 units in 16 plants around the world.

Some of the disadvantages of gas compression from atmospheric pressure was overcome by the development between 1933/36 of the Lurgi process. This is somewhat offset by the high methane content of the gas produced as well as the need for extra equipment to deal with naphthas, tars and phenols which appear as by-products. To date, about 63 units in 13 plants have been put into operation and there has been considerable interest in the pilot plant work carried out on the Lurgi plant in Westfield Scotland to methanate the gas to produce SNG.

Where oxygen and steam are used as the gasification medium, the Koppers-Totzek process can handle most types of coal in the entrained fuel gasifier which requires pulverized fuel. The higher temperature of gasification, 2200°F, results in no heavy hydrocarbon being carried forward, and the gas, after purification, can be utilized for production of methanol or ammonia. Fifty-two units of this type have been reported in 20 plants worldwide.

Although there are many other processes in different stages of development, it can be seen that coal gasification is not a new and untried field of operation and indeed as recently as 1955 has been used for the production of synthesis gas in the U.S.

To prepare the raw gas from the gasification section for methanol synthesis requires several additional processing steps, namely:

1. compression
2. shift conversion
3. acid gas removal

all of which have been in commercial operation for many years. Each of these processing steps can be found in any modern day ammonia or methanol plant, regardless of the feedstock being processed.

The exact combination of process steps to convert coal to methanol will vary depending upon the gasification scheme selected and the economics of by-product production. Figures 1, 2, 3 and 4 present four possible alternatives.

As a typical example, the following (see Figure 5) is a more detailed description of a methanol from coal facility based on the Winkler gasification technology available from Davy Powergas:

Winkler Coal Gasification

Coal Preparation. The run-of-mine coal from storage pile is conveyed to the crushers where the coal is crushed to a particle size of $3/8" \times 0$. If predrying of the coal is required, fluid bed dryers may be utilized to reduce the moisture level to that required. In the dryer, hot air, heated by the combustion of coal, is used to fluidize the coal and supply the heat necessary for drying. Most of the dried coal is removed directly from the fluid bed. However, a portion is entrained in the hot gases leaving the dryer. A cyclone recovers most of the entrained coal, and it is returned to the dryer product coal and conveyed to the gasification section. The hot gases from cyclone are scrubbed with water for particulate matter removal before venting to atmosphere.

Coal Gasification. The coal feed is conveyed to the gasifier through lock hoppers and screw conveyors. The gasifier is maintained as a fluidized bed operation under moderate pressure. A mixture of steam and oxygen is injected at several points within the bed to gasify the coal while steam alone is injected into the bottom most level to fluidize the coal and to cool the larger ash particles discharging from the gasifier bottom. The high bed temperatures, typically 1700-2200°F, are obtained by the partial combustion of the coal's carbon and contained hydrocarbons. Due to the relatively high temperature of gasification, the tars, gaseous hydrocarbons and carbon present in the coal are converted to carbon monoxide, hydrogen, and carbon dioxide. Only a small percentage of methane remains in the raw product.

The primary coal gasification reactions are:



At a constant coal feed rate to the Winkler generator, the ratio of oxygen and steam to coal is controlled to maintain the desired bed temperature. Optimum bed temperature is a compromise between product gas calorific value, carbon efficiency and overall thermal efficiency, but is limited by the ash softening temperature. If the ash softening temperature is exceeded, the ash may fuse and agglomerate, thus upsetting the fluidization characteristics of the bed and possibly plugging the reactor.

As a result of the fluidication, the particles of ash and their contained carbon are segregated according to size and specific gravity, i.e., the heavier particles fall down through the fluidized bed and pass into the ash discharge unit at the bottom of the generator while the lighter particles are carried up out of the bed by the product gas. Approximately fifty to seventy-five percent of the incoming ash will be entrained in the hot product gases leaving the top of the Winkler generator. The exact quantity entrained with a given gas velocity, is primarily dependent upon the particle size distribution of the feed coal. Since the height of the fluidized bed is relatively small compared to the total height of the generator, the upper or major portion of the generator is available to perform two other functions; firstly, to further gasify any entrained carbon particles, and secondly, to effect a separation of any heavier solid material. To aid this further gasification, a portion of the steam and oxygen is added to the generator near the upper limit of the fluid bed.

The unreacted carbon in the discharged ash is a function of gasifier temperature and coal reactivity. Generally, reactivity varies inversely with geological age, lignites being the most reactive.

Gas Cooling and Particulate Removal

The hot gases leaving the generator pass through the heat recovery train where heat is removed from the gas by generating and super-heating high pressure steam and preheating boiler feedwater. The hot Winkler product gas is cooled to approximately 300°F in the heat recovery train. High pressure steam in excess of that required by the process is generated and therefore available to drive the product gas compressors and/or the compressors in the air separation plant.

The heavier char particles leaving the bottom of the gasifier pass out of the system and the balance of the char is carried out of the gasifier in the overhead product gas. The bulk of this char is removed in the heat recovery train and in cyclones. In combination, the heat recovery train and cyclones are designed to remove approximately 85% of the entrained solids. The char thus removed will be utilized as supplementary fuel in the boiler house. The gas from the cyclone flows through the venturi scrubber where the remaining char is removed to a level of 1 grain/1,000 SCF.

Production of Methanol

The methanol plant contains the following sections to process the raw gas from the coal gasification plant:

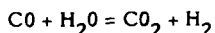
1. Raw Gas Compression
2. Gas Shift Conversion
3. Acid Gas Removal

4. Methanol Synthesis and Purification
5. Sulfur Recovery
6. Oxygen Production for Coal Gasification
7. Offsites

A description of each section is as follows:

Raw Gas Compression. The methanol synthesis is conducted at approximately 100 Ats. and it has been found that it is more economical to compress the gas exiting the gasification unit prior to further processing. The cooled and the dust free gas from the coal gasification section is compressed to 1480 psig in steam turbine driven compressors.

Gas Shift Conversion. The purpose of the shift conversion step is to adjust the ratio of carbon monoxide to hydrogen to that required for the methanol synthesis according to the exothermic shift reaction:



An exit CO content of 6.4 volume percent in the shifted gas is achieved in a one stage shift conversion reactor and a part of the compressed gas is by-passed around the shift reactor, cooled and mixed with the cooled shift effluent to yield an average CO content of approximately 20%. The compressed gas to the shift reactor is mixed with the shift reaction steam to give a 1.0 ratio of steam to the dry gas and preheated by heat exchange with the hot effluent gases from the shift reactor prior to its introduction to the reactor which contains a sulfur resistant catalyst. From the interchanger, the shift effluent is cooled in a series of waste heat recovery exchangers.

Acid Gas Removal. The Rectisol process has been selected to remove the acid gases as it has the advantage of using the plant product as the scrubbing medium. This process was developed by Linde and Lurgi in Germany and plants presently in operation have been designed by both companies.

The Rectisol process absorbs CO_2 and H_2S from the shifted synthesis gas stream using methanol. CO_2 is rejected to the atmosphere and a hydrogen sulfide rich gas is available for the sulfur recovery in a Claus Plant. These streams are obtained by selectively regenerating the methanol from the absorber in a two stage regenerator system. Low pressure nitrogen from the air separation section is used to strip carbon dioxide from the rich methanol solution in the first stage regenerator. Stripped solution from the first stage regenerator is stripped of its hydrogen sulfide by a steam heated reboiler in the second stage regenerator. The H_2S stream flows to the Claus unit for sulfur recovery and the purified synthesis gas is now ready for methanol synthesis. The carbon dioxide content of the synthesis gas is controlled by mixing a desulfurized side stream of high carbon dioxide content from the absorber with the absorber overhead.

Methanol Synthesis and Purification. The unique feature of this process is the synthesis step, utilizing a copper based catalyst specially developed by ICI, which gives good yields of methanol at low temperatures (410°F to 520°F). The high activity of the catalyst at low temperature permits the reaction to be carried out at pressures as low as 750 psig and is the key to the economy of the process. By-product formation is minimized as a result of the low operating temperature, thus leading to high process material efficiencies.

Final traces of sulfur are removed from the synthesis gas by a bed of zinc oxide after preheating to desulfurization temperature. A bed of chloride catch is also provided to prevent chloride poisoning of the synthesis catalyst. After cooling, the make-up synthesis gas enters the synthesis loop at the inlet of the circulator compressor. The mixture of unconverted gas and fresh make-up gas is preheated to reaction temperature in the converter interchanger by the hot gases leaving the converter. The methanol synthesis converter is a pressure vessel containing a single bed of catalyst. Temperature control is effected by injecting cold gas at appropriate levels into the catalyst bed.

The feed gas and the cold shot gas combine and react to form methanol as they pass downwards over the catalyst. The converter exit gas is first cooled in the converter interchanger and subsequently in the crude methanol condenser where the crude methanol product is condensed. Crude product is separated in the high pressure separator.

The non-reactive components of the make-up gas, methane and nitrogen are purged from the synthesis loop between the separator and the point of make-up gas addition and are subsequently used as boiler fuel.

The crude methanol collected in the separator is let down in a single stage to the let down vessel and the resultant product passes to the distillation plant. To provide some independent operation of the synthesis and distillation units, the crude can alternatively be pumped to crude methanol storage.

Flash gas from the letdown vessel (mostly dissolved gases) is mixed with the synthesis loop purge stream and used as fuel.

The crude methanol is processed in a single column system to fuel grade methanol, and the overall efficiency of the distillation system is expected to be 99% at the end of life conditions.

The upper section of the column removes the light ends, principally dimethyl ether, methyl formate, aldehydes, ketones, and lower paraffin hydrocarbons while the sections of the column below the feed tray is designed to remove water. Fusel oil (predominately alcohols such as isobutanol) is purged from a tray near the base of the column. In order to reduce organic and thermal losses in the effluent water stream, the fusel oil is subsequently blended back into the product fuel grade methanol. The fusel oil may be utilized as fuel if chemical grade methanol is the desired product.

Methanol product is removed from the top section of the column, cooled, and pumped to storage.

Sulfur Recovery. Sulfur recovery will be accomplished in a standard Claus unit equipped with a Wellman-Lord SO_2 recovery unit. The W-L system has been included so that the tail gas leaving the plant will be in compliance with environmental regulations.

Oxygen Production. The methanol plant of 5000 TPD capacity from coal requires large tonnage oxygen for coal gasification and, hence, it is economical to include an oxygen production unit in the facilities. Standard cryogenic air separation units producing 1600 TPD of oxygen can be used. The by-product nitrogen from this unit will be utilized in the plant for purging, char conveying and rectisol unit methanol stripping.

Offsites. The offsites section consists of those facilities to provide all services to the other sections. The major systems are water treatment, cooling tower, boiler feedwater, and the coal fired high pressure boilers. The coal fired boiler is a conventional pulverized coal boiler, but will also burn the purge gases from the methanol loop and all of the dry char from the Winkler gasifiers. The boiler package includes an electrostatic precipitator for particulate removal, but does not include facilities to remove sulfur dioxide from the boiler flue gases.

Design Basis

Product Specifications

Fuel Grade Methanol

Analysis

Methanol plus organics, Wt. %	99.5 minimum
Water, Wt. %	0.5 minimum
Higher heating value, BTU/lb.	9,725

Conditions

State	Liquid
Pressure, psig	100
Temperature, °F	110
Delivered to Battery Limits for storage	

Raw Material Specifications

Coal

Ultimate analysis, Wt. %

Water	16.50
Ash	18.87
Carbon	48.36
Hydrogen	3.61
Nitrogen	0.86
Sulfur	0.57
Oxygen	<u>11.23</u>
Total	100.00

Higher heating value, Dry, BTU/lb.	10,345
Ash softening point, °F	2,282
Ash melting point, °F	2,597
Ash flow point, °F	2,723

Raw Material, Utility and Product Rates

When producing the design 5,000 TPD of methanol (99.5% purity), the battery limit flows for the unit herein described are as follows:

Imports

Coal

Process Coal	M lb/hr	896
Boiler Coal	M lb/hr	<u>129</u>
	Total	1,025
Raw Water	M lb/hr	3,047
Electric Power	MKWH	57
NaOH	lb/hr	45

Exports

Methanol	ton/hr	208
Sulfur	ton/hr	2
Wet char	M lb/hr	27
Boiler Ash	M lb/hr	52
Water Effluent	M lb/hr	<u>1,300</u>

DAILY OPERATING COST DATA

Methanol Production, S Tons/Day	5,000
---------------------------------	-------

	<u>Unit Cost</u>	<u>\$/Day</u>
Raw Water	1.5¢/1,000 lb	1,097
Electric Power	1¢/KWH	13,637
Caustic Soda	6¢/lb	65
Total, \$/Day		14,799
Coal	\$3/S Ton	36,913
	\$6/S Ton	73,825
	\$9/S Ton	110,738
	\$12/S Ton	147,650
	\$15/S Ton	184,563

No credit has been taken for sulfur production.

Economics

Using the design just described, a capital estimate of the facility was made based on January 1975 prices and the following overall economics were calculated:

Capital Cost, MM\$	270	
No. Gasifier Trains	8	
No. Operators/Day (4 shifts)	80	
		<u>\$/Day</u>
Maintenance Materials & Labor @ 4%		32,700
Taxes & Insurance @ 2.5%		20,500
Administrative Overhead @ 2.5%		20,500
Oper. Labor & \$10,000/Manyear		2,400
Capitalization		
Utility		
- 65% Debt @ 10%	62,500	
- 35% Equity @ 12% DCF	62,400	
- Incl. 20 yr Straight Line Dept.		
Total Fixed Charges, \$/Day		201,000
Total Fixed Charges, \$/ST MeOH		40.20
Total Direct Charges, \$/ST MeOH		2.96
Coal	\$3/ST, \$/ST MeOH	7.38
	\$6/ST, \$/ST MeOH	14.77
	\$9/ST, \$/ST MeOH	22.15
	\$12/ST, \$/ST MeOH	29.53
	\$15/ST, \$/ST MeOH	36.91

PRESSURIZATION OF THE WINKLER PROCESS

The Winkler process for the gasification of coal has provided gas for fuel or power, for synthesis of methanol and ammonia, for Bergius-Hydrogenation, and for the production of hydrogen in Europe and Asia when coal was the only raw material available. All of those commercial installations were designed and operated so that, after cooling and particulate removal, the product gas would be delivered at nominally atmospheric pressure. The reason for the low pressure operation was that, at that time, German regulations favored atmospheric pressure plants, i.e., operating pressures above 1.5 ata (7 psig) created problems in the areas of materials and government supervision.

In mid 1972, Davy Powergas undertook a study to determine whether or not a Winkler gasifier operating under these proven conditions would be competitive with other available technology. Within the accuracy of the estimates made, none of the commercial processes appeared decisively better than any of the others and hence, review was begun of the Winkler process to determine what constituted its limitations for current U.S. conditions. It became rather obvious that the biggest deficit was the low pressure of operation since the detrimental effects of low pressure operation are threefold:

1. Large size equipment to handle the large volume of gas.
2. High capital cost attributable to the product compression station.
3. High daily operating cost of power for product compression

Process economic studies were conducted to find the optimum pressure ranges and to assess the magnitude of savings attributable to pressure operations. Three separate studies were completed as defined below:

- Case I - Effect of gasification pressure on the production cost of low/medium BTU fuel gas using air/oxygen as the gasifying medium. The final fuel gas is delivered at 210 psig, with a maximum of 100 ppm of sulfur.
- Case II - Effect of gasification pressure on the production cost of 5,000 STPD of methanol.
- Case III - Effect of gasification pressure on the production cost of 1200 STPD of ammonia.

The general conclusions were encouraging as outlined below.

1. General Conclusions

It may be concluded that an increase in gasifier operating pressure results in a decrease in the overall cost of product. It becomes apparent that the greatest savings may be attributed to a decrease in the number of gasification trains required for a given output. Although there are significant savings in the compression requirements for the higher pressure case, the number of gasifiers remains constant. Despite the fact that the size of each gasifier has decreased, the increase in cost of the higher pressure design outweighs the net savings in compression, resulting in a slight increase in overall production cost.

The greatest decrease in the number of gasifiers occurs between 20 psia and 43 psia, for example, the plant for the production of 5,000 ST/D of methanol would require 12 gasifiers at 20 psia as compared with 8 at 43 psia.

From examination of graphs, it was deduced that the optimum operating pressure for the gasifier, depending upon the final product, lies between 120 and 180 psia. The one case which does not necessarily follow these conclusions is the integration of a Winkler system with a combined cycle power plant. In this case the air compression is provided by the gas turbine--compressor system, and as a result, the optimum gasification pressure is the highest permitted by the air delivery pressure.

2. Methanol Systems

Figures 6 and 7 present the cost of producing 5,000 ST/D of methanol from western sub-bituminous coal. Since methanol may be considered either a bulk chemical, or a liquid chemical fuel, the production costs reflect both typical utility financing (Figure 6) and typical industrial financing (Figure 7). Although there are but small savings in production cost over the range of gasifier pressures of 43-213 psia, the minimum production cost occurs at approximately 150 psia generator pressure.

The improvement in capital and operating costs resulting from pressurization is shown clearly in Figure 8 which also compares alternative processes such as steam reforming and partial oxidation for the production of synthesis gas.

ACKNOWLEDGEMENTS

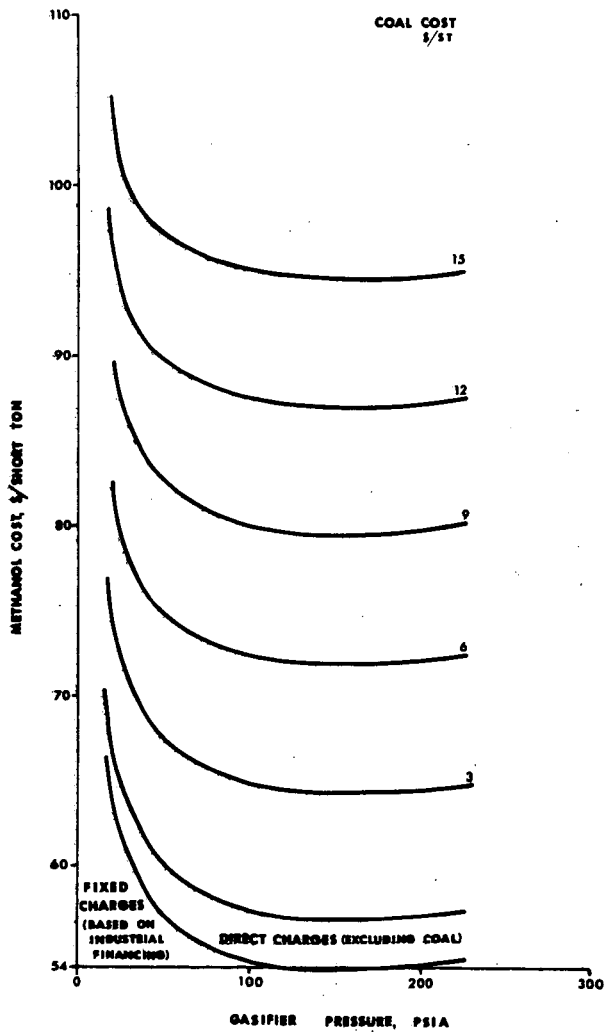
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REFERENCES CITED

1. H. R. Linden - Southern Gas Association Meeting
Houston, April 23, 1974.
2. Press Release April 17, 1975, Power & Marine Systems,
Farmington, Connecticut.
3. M. L. Kastens, J. F. Dudley & J. Troeltzsch
Ind. Eng. Chem 40 2230 1984.
4. R. M. McGee - Engineering Foundation Conference
New Hampshire, July 1974
5. G. E. Harrison, "Fuels of the 1980's & 1990's",
London Chemical Engineering Congress, May 14, 1975.

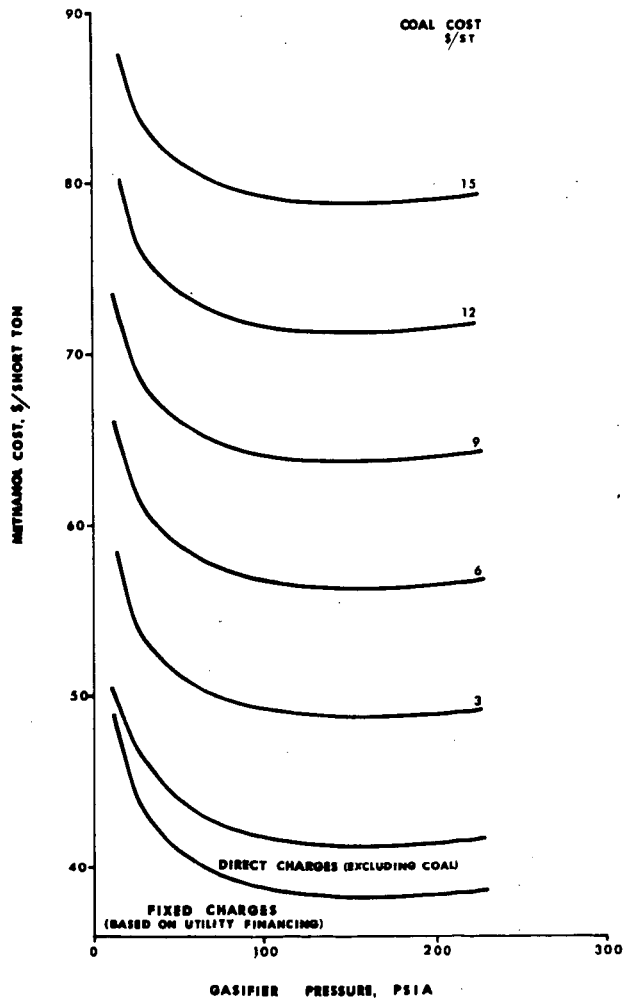


GRAPH 4

METHANOL FROM COAL
BY THE WINKLER PROCESS

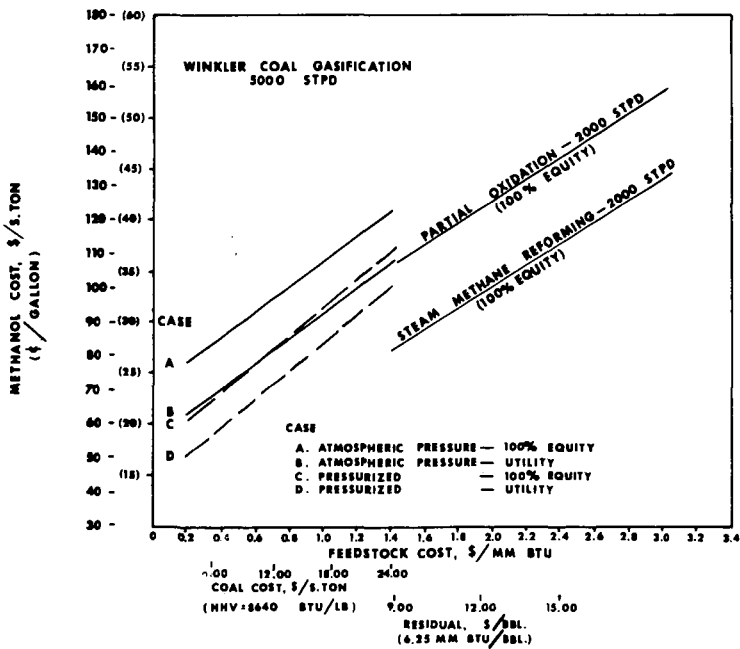


GRAPH 3

METHANOL FROM COAL
BY THE WINKLER PROCESS


Davy Powergas

COST TO PRODUCE METHANOL BY ALTERNATIVE PROCESSES



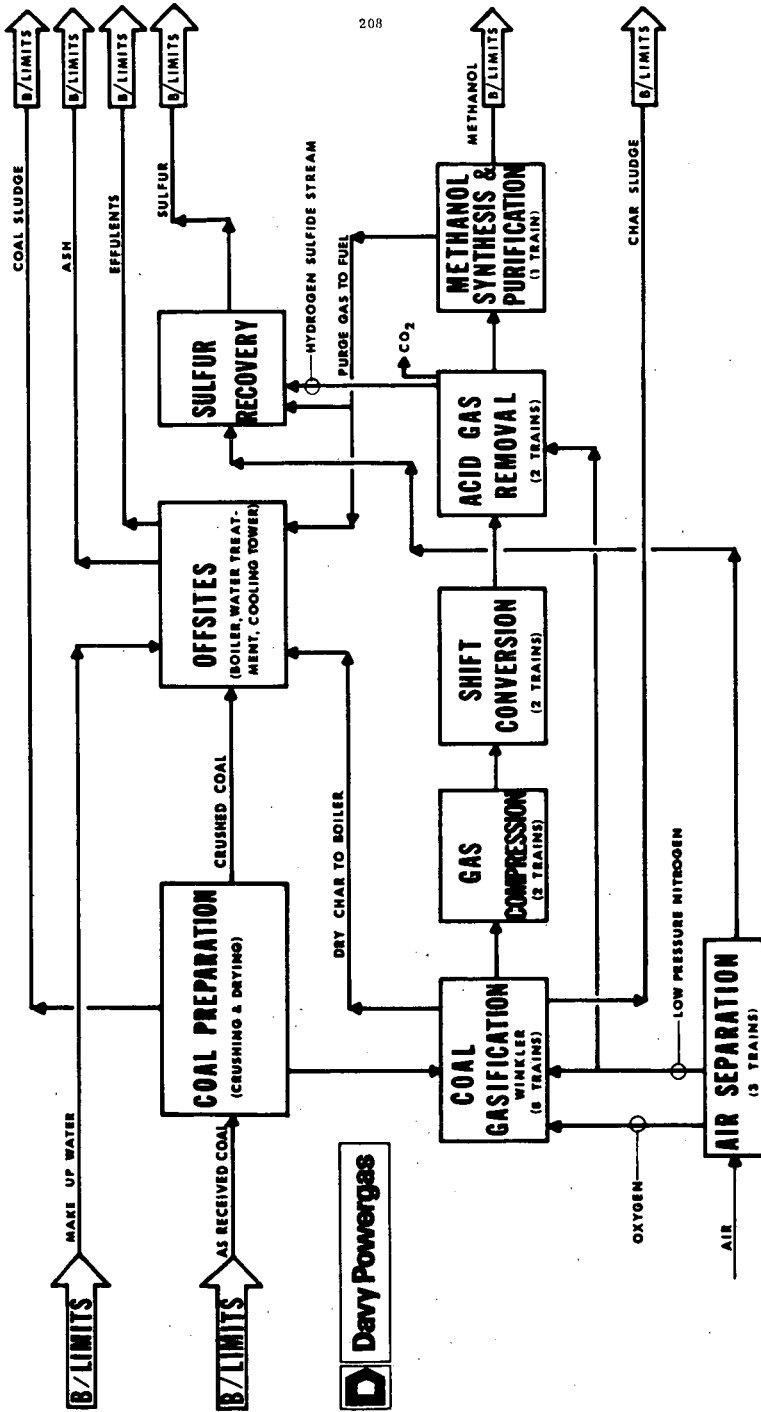


Fig. 5 Typical Methanol From Coal Facility Based On Winkler Gasification.

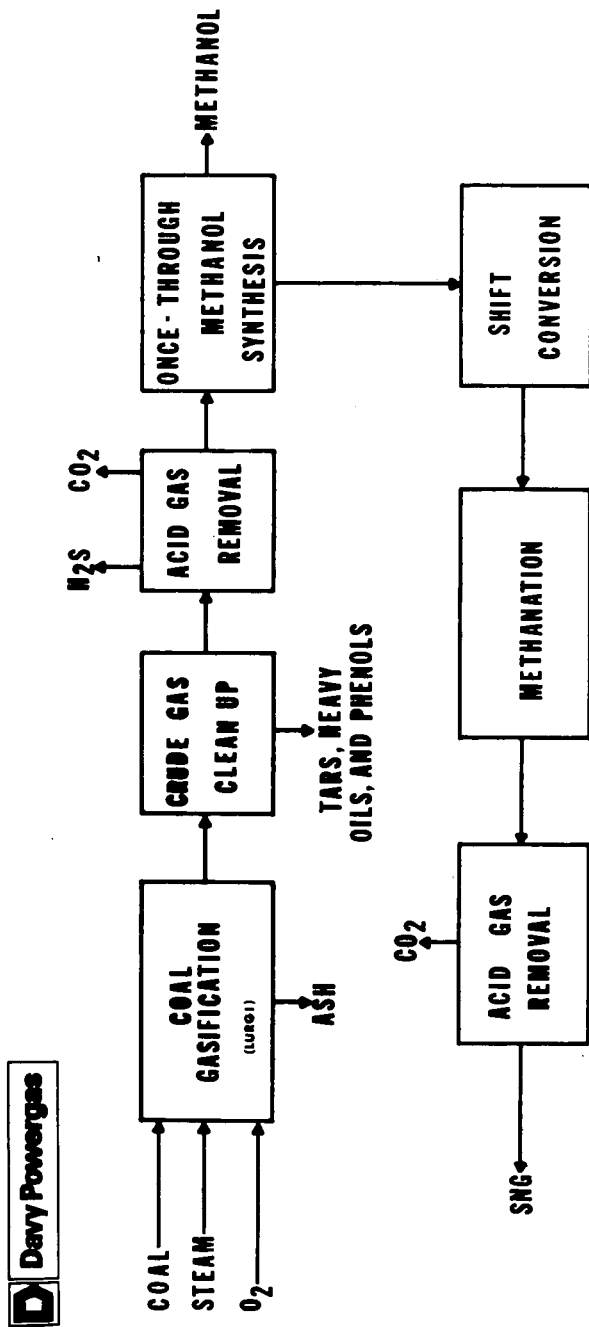


FIGURE 4

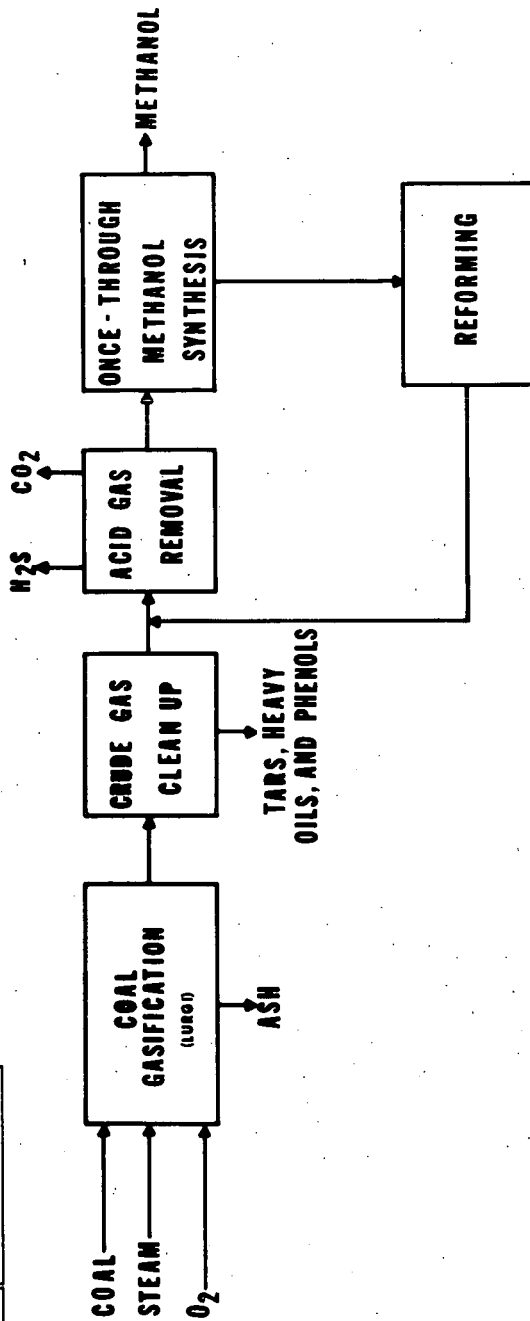


FIGURE 3

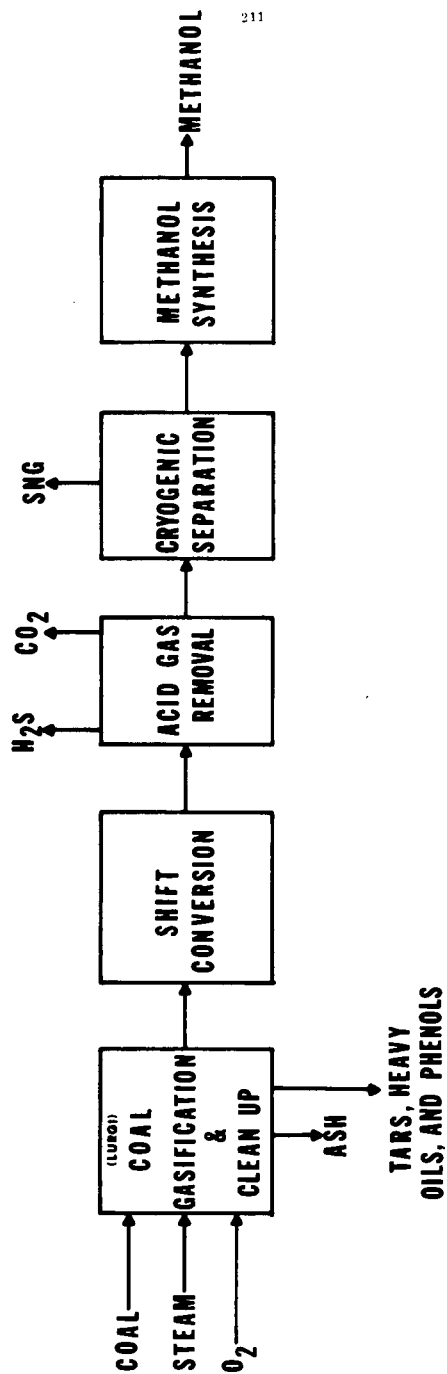


FIGURE 2

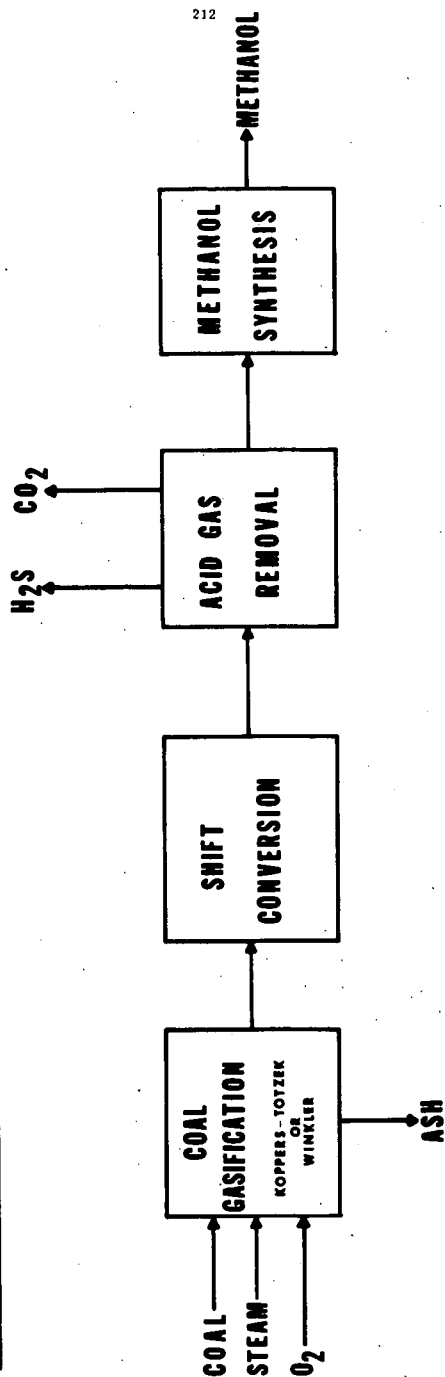


FIGURE 1